

**Preliminary Models of the Fate and Bioaccumulation of
Selected Chemicals in the Salt Marshes of the
LCP Superfund Site, Brunswick GA.**

July 3, 2001

Report prepared for:

**Stratus Consulting Inc.
PO Box 4059
Boulder, Colorado 80306-4059**

Report prepared by:

**Brendan Hickie PhD
Trent University
Peterborough, Ontario
Canada K9J 7B8**

**(705) 748-1421
bhickie@trentu.ca**

Table of Contents

1.0.	Introduction	1
2.0.	Fate Modelling for Aroclor 1268 and Selected PAHs	2
2.1.	Site Description Relevant to Model Formulation	2
2.2.	Model Description	2
2.3.	Parameters, Baseline Values, Uncertainty, Sensitivity	8
2.4.	Chemical Characteristics	10
2.5.	Outline of Simulations	12
2.6.	Results and Discussion	12
3.0.	Bioaccumulation Modelling	23
3.1.	Bioaccumulation of Aroclor 1268	25
3.2.	Bioaccumulation of PAHs	28
4.0.	Conclusions	34
5.0.	References	35

Tables

Table 1.	Definition of Z values, notation terms and standard units used in the model.	4
Table 2.	Process D values and rate expressions used in the model.	6
Table 3.	Physical and hydrological characteristics of the Purvis Creek salt marsh used as baseline values in the LCP-QWASI model.	9
Table 4.	Physical and chemical properties of selected chemicals at 25°C and their estimated half lives (hours) in air, sediment and water.	11
Table 5.	Pre-removal chemical concentrations in water and sediments of the Purvis Creek salt marsh used as initial values in the LCP-QWASI model.	12
Table 6.	Results of limited sensitivity /uncertainty analysis for Aroclor 1268 in the dynamic LCP-QWASI model.	17
Table 7.	Summary of results from the pre-removal and post-removal fate model simulations for Aroclor 1268.	18
Table 8.	Summary of results for baseline modelling of total PAHs using the physical chemical properties of three selected PAHs.	21
Table 9.	Data requirements for bioaccumulation model.	23
Table 10.	Species characteristics and feeding preferences used in the preliminary model simulations based on summaries from the Marine and Coastal Species Information System (MACSIS, 1998) and from Sprenger et al (1997).	24
Table 11.	Summary of conditions used in the food web bioaccumulation model simulations for PAHs.	31

Figures

Figure 1.	Aerial photograph showing the boundaries of model segments in the salt marsh.	3
Figure 2.	Flow chart showing segments, compartments and pathways of the Purvis Creek marsh contaminant fate model.	4
Figure 3.	Processes treated in each QWASI model segment.	7
Figure 4.	Simulated changes in Aroclor 1268 concentrations in sediment and water of each model segment and mass in the sediments using the baseline data set and pre-removal sediment concentrations.	14
Figure 5.	Overall flux rates of Aroclor 1268 (g/day) for the four combined segments after one year of the simulation using the baseline data set.	15
Figure 6.	Simulated changes in Aroclor 1268 concentrations in sediment and water of each model segment and mass in the sediments using the baseline data set and post-removal sediment concentrations.	19
Figure 7.	Simulated changes in total PAH concentrations in sediment and water of each model segment using the physical chemical properties of fluoranthene.	22
Figure 8.	Diagram of the aquatic components of the salt marsh food web considered in the bioaccumulation model.	24
Figure 9.	Predicted sediment:water concentration ratio (ng/g sediment dry wt ÷ ng/L water) from the baseline fate model simulations for Aroclor 1268 initiated with the (A) pre-removal, and (B) post-removal sediment concentrations.	26
Figure 10.	The effect of varying the sediment:water concentration ratio (ng/g sediment dry wt ÷ ng/L water) on the model-predicted BSAFs for Aroclor 1268.	27
Figure 11.	Predicted Aroclor 1268 BSAF values for organisms in the simplified salt marsh food web assuming equilibrium partitioning for benthic infauna (default Gobas model; BSAF = 1.0) and assuming a reduced BSAF of 0.4 for benthic infauna (revised model).	27
Figure 12.	Comparison of predicted tissue concentrations with concentrations measured in organisms (☒) from various locations in the Purvis Creek marsh.	28
Figure 13.	Predicted sediment:water concentration ratios (ng/g sediment dry wt ÷ ng/L water) for the three example PAHs derived from the baseline fate model simulations initiated with the pre-removal sediment concentrations.	30
Figure 14.	Predicted concentrations of phenanthrene, fluoranthene and benzo(a)pyrene for organisms in the Purvis Creek marsh derived from the simulations outlined in the text and Table 11.	32

1.0. Introduction

This project included two components. The first was to construct a preliminary model of the fate and mass balance of Aroclor 1268 and total PAHs in the Purvis Creek salt marsh adjacent to the LCP industrial site in Brunswick, GA. This was achieved by developing and applying a fugacity-based dynamic multi-compartment mass balance model which considers chemical fate in sediments, water and air. The model was based on the well established Quantitative Water-Air-Sediment Interactive lake model (QWASI) originally developed by Mackay *et al.* (1983). The model was used to estimate the changes in chemical concentrations in sediment and water in the marsh, the half life of the selected chemicals and the export of chemicals from the marsh to the adjacent Turtle River.

The second component of the project was to construct a preliminary model of the bioaccumulation of Aroclor 1268 and selected PAHs through the aquatic component of the marsh food web (i.e. excluding birds and mammals). Aroclor 1268 accumulation was modelled using the Gobas food web accumulation model (Gobas, 1993).

The models and their results should be considered as preliminary evaluations of this system. The models were constructed using limited site-specific data and information. These were supplemented by parameter values from the literature or, when necessary, by assumed values. Nevertheless, the models and results can provide insight into the fate, transport and bioaccumulation processes at the site, and can help identify and prioritize key data gap areas where additional work could be conducted.

While mercury is an important contaminant at the LCP site, development of mercury fate and bioaccumulation models is not feasible because of the lack of sufficient site-specific data. For example, mercury fate and bioavailability are largely driven by its speciation in water and sediment, yet site-specific data on speciation (Hg^0 , Hg^{2+} , meHg) and the factors that control it (e.g. pH, DOC, salinity, sediment oxygen, etc) are not available. Thus, any effort to model mercury without such critical site-specific data would be prone to extreme uncertainty.

Chemical Fate and Mass Balance Modelling

A mass balance model has been developed and calibrated to describe the fate and transport of selected chemicals (Aroclor 1268, and three representative PAHs covering a range of physical chemical properties) in the water and sediments of the salt marsh system adjacent to the LCP industrial site in Brunswick GA. The model is a dynamic version of the QWASI model and is applied here to estimate the rate of chemical transport from contaminated marsh sediments to the adjoining Turtle River and to identify critical parameters and processes. The marsh was divided into four segments with water and sediment compartments having areas and volumes calculated using GIS. Four segments were deemed appropriate based on interpretation of aerial photographs and elevation data for the area. The segments are connected by advective tidal water flows to and from the Turtle River. The model also includes a single atmospheric compartment and allows for air-water exchange (although this process is negligible for the chemicals considered). Processes treated include sediment-water exchange and sediment burial, advective transport in water, degrading reactions in water and sediment, and air-water exchange (evaporation, wet and dry deposition). Chemical concentrations in the air and inflow water from the Turtle River are assumed to be at constant background levels over the duration of simulations. Emissions and advective inputs of chemical from the area surrounding the marsh are assumed to be negligible. Thus, the primary output from the model is an account of the decline in the inventory of chemical over time from the marsh by the various pathways considered, including transport to the Turtle River. The output, directed to ASCII text files at specified intervals, includes chemical concentrations in water and sediment of each segment and a summation of the relevant mass fluxes.

Food Web Bioaccumulation Modelling

The aquatic food web bioaccumulation model developed for Lake Ontario by Gobas (1993) was adapted to simulate the bioaccumulation of Aroclor 1268 and the three representative PAHs from water and sediments through the salt marsh foodweb. The Gobas model is widely used (e.g. U.S EPA, 1995), is similar to other steady-state food web models (Thomann et al., 1992; Campfens and Mackay, 1997), but has fewer data requirements. For small organisms (e.g. phytoplankton, zooplankton, small benthic infauna) chemical concentrations are assumed to result from equilibrium partitioning from water or sediment. For larger organisms (e.g. fish, macroinvertebrates), chemical concentrations are estimated from the balance of chemical uptake from water and food, and losses by respiration, egestion, biotransformation and growth dilution. The model includes a simplified salt marsh food web which was constructed to include species used in past contaminant monitoring studies (Sprenger et al 1997; Maruya and Lee, 1998a,b). These include fiddler crab (*Uca sp.*), grass shrimp (*Palaemonetes pugio*), blue crab (*Callinectes sapidus*), and fish such as killifish (*Fundulus heteroclitus*) and red drum (*Sciaenops ocellatus*). The model is applied here to estimate the accumulation potential of the selected chemicals through the food web with particular attention to the biota-sediment accumulation factor (BSAF).

2.0. Fate Modelling for Aroclor 1268 and selected PAHs

2.1. Site Description Relevant to Model Formulation

The Purvis Creek salt marsh was divided into four model segments based on physical site information and on the distribution of contaminants in sediments (Figure 1). The segments were designated as 1) Purvis Creek, 2) Upper Marsh, 3) LCP Marsh, and 4) Lower Marsh. Segment 1 receives initial tidal inflow water from the Turtle River during rising tides, portions of which flow into the other three segments. On falling tides the flow is reversed, passing from the three "marsh" segments to the creek segment and out to the Turtle River. Thus, the water flow rates and volumes in each segment vary over the course of each tidal cycle lasting just over 12 hours. The average tidal amplitude near the mouth of Purvis Creek is about 7.8 feet (2.4 metres) (NOAA, 2000). While a dynamic hydrologic tidal submodel could be developed for the marsh a simpler, but ultimately equally effective, approach was taken which treated the system as if there were a continuous water flow through the marsh. The flow rates were calculated to match the volume of water moving into and out of the marsh on a daily basis. Specific characteristics of each model segment (surface area, volume, water flow rate etc) are described below (section 2.3)

2.2. Model Description

The model (LCP-QWASI) consists of a single atmospheric compartment and the marsh system which consists of four segments, each of which contains a water and sediment phase (Figure 2). In total there are then nine compartments or "boxes", each of which is treated as being well-mixed.

The marsh component of the model is a four segment version of the QWASI fugacity model developed by Mackay *et al.* (1983) and previously applied to freshwater and marine systems by Mackay (1989), Mackay and Southwood (1992), Lun et al (1998) and Mackay and Hickie (2000). The use of fugacity as a surrogate for concentrations has been reviewed by Mackay (1979, 1991) and Paterson and Mackay (1985). Briefly, fugacity, f in units of Pa, is a measure of a chemical's partial pressure or "escaping tendency". It is logarithmically proportional to chemical potential and thus is essentially linearly related to concentration, C (mol/m³) through a proportionality constant termed the fugacity capacity or Z (mol/m³•Pa). Z is a function of the nature of the chemical properties of the medium in which it is present and of temperature (Table 1). The Z value of a chemical in a compartment is deduced using a dimensionless partition coefficient, K_{12} between phases 1 and 2, which is the ratio of Z values (i.e., Z_1/Z_2) between the two compartments.

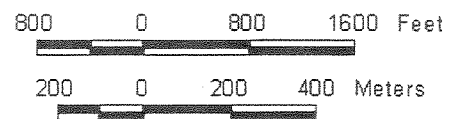


Figure 1. Aerial photo of the Purvis Creek Saltmarsh showing the boundaries of the four model segments.

h:\role c\l\p\2015_01\16\fig1.jpg

Table 1. Definition of Z values, notation terms and standard units used in the model.

Compartment	Definition of Z (mol/m ³ •Pa)	
Air	$Z_A = 1/RT$	$R = 8.314 \text{ Pa} \cdot \text{m}^3 / \text{mol} \cdot \text{K}$ $T = \text{temperature in K}$
Water	$Z_W = 1/H = C^S / P^S$	$H = \text{Henry's law constant (Pa} \cdot \text{m}^3 / \text{mol)}$ $CS = \text{Aqueous solubility (mol/m}^3)$ $PS = \text{Vapor pressure (Pa)}$
Sediment or Suspended Particles	$Z_S = K_{SW} \rho_S / H$	$K_{SW} = \text{Partition coefficient (L/kg)}$ $\rho_S = \text{Phase density (kg/L)}$
Aerosols	$Z_Q = Z_A K_{XA} = 6 \times 10^6 / P_L^S RT$	$P_L^S = \text{Subcooled liquid vapor pressure}$
Z for Bulk Water	$Z_{WT} = Z_W (1-VFP) + Z_P VFP$	$VFP = \text{Volume fraction of suspended particles}$ $Z_P = Z \text{ for suspended particles}$
Z for Bulk Sediment	$Z_{ST} = Z_W (1-VFP) + Z_S VFP$	$VFS = \text{Volume fraction of sediment solids}$
Z for Bulk Air	$Z_{AT} = Z_A (1-VFQ) + Z_Q VFQ$	$VFQ = \text{Volume fraction of aerosols}$

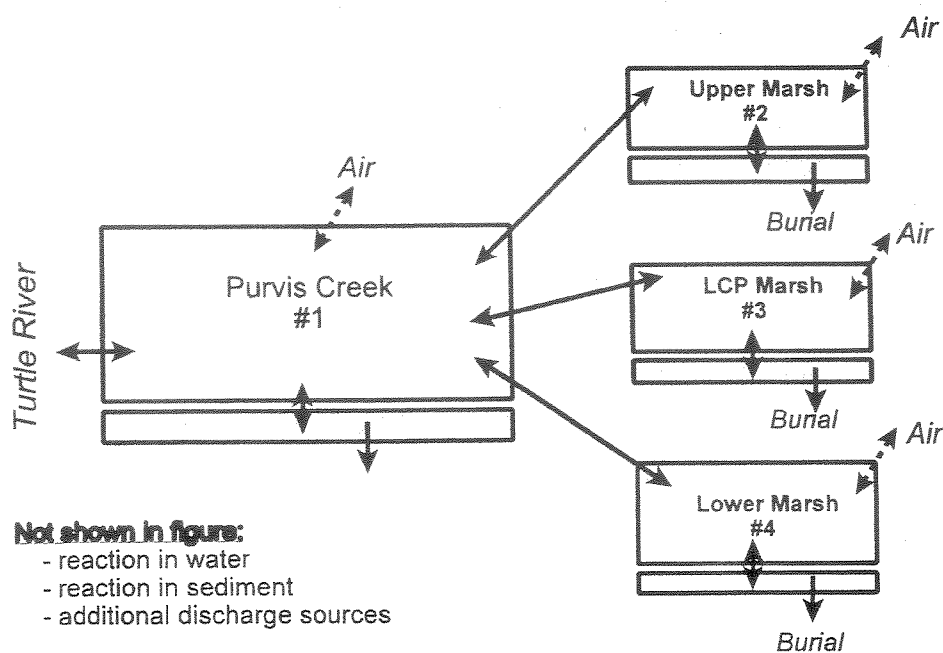


Figure 2. Flow chart showing segments, compartments and pathways of the Purvis Creek marsh contaminant fate model.

The atmospheric compartment receives air inflow assumed to contain "continental" background concentrations of Aroclor 1268 and PAHs (local emissions are considered to be negligible in this case). Chemicals in this compartment are subject to losses by advective transport from the air mass (i.e., loss in wind), degrading reactions and wet and dry deposition to the marsh. Calculation of the latter loss process rates requires an estimate of air-aerosol partitioning of the chemical, which is calculated from the sub-cooled liquid vapor pressure described by Mackay (1991). Chemical evaporation from the marsh is assessed as a loss process in the model, but is not included as an input to the air because it would only make a minor contribution to the atmospheric compartment mass balance. This results in an insignificant error in the overall chemical mass balance but eliminates some excessive algebraic complexity from the model.

Rates of intermedia transport and transformation processes are evaluated using a group of transport parameters termed D values in units of mol/hPa which are defined in Table 2. The process rates (also referred to as flux rates) in or from a phase are expressed as products of f and D, i.e., Df (mol/h). In this paper, D values are used for advective flow, diffusive flow, reaction and deposition processes.

The basic unit of the QWASI model, as shown in Figure 3, consists of three compartments: a well-mixed sediment compartment underlying a well mixed water column which is exposed to the atmosphere. Bulk phase Z values are calculated for the three primary media which also include the contribution of dispersed phases within each media. The air compartment is treated as an air-aerosol mixture, water as water plus suspended particles and sediment as solids plus pore water. The overall model for the Purvis Creek - LCP Marsh consists of four such water-sediment compartments, as described above.

In dynamic versions of QWASI, as is used here, differential mass balance equations can be written in terms of fugacity and D values previously defined for each of the water and sediment segments. The differential equation describes the change in chemical mass (VZf) or fugacity (f) in a specific compartment as the balance of the combined accumulation and loss processes affecting the chemical in that phase. The equation takes the general form:

$$dVZf/dt = (\text{sum of mass inputs}) - (\text{sum of mass losses}) \quad (1)$$

$$df = dt/VZ * ((\text{sum of mass inputs}) - (\text{sum of mass losses})) \quad (2)$$

Thus, for water compartments

$$df_w = \frac{dt}{VZ} * ((E_w + f_A D_A + f_S D_{SW} + \sum f_{wi} D_i) - f_w (D_w + D_{ws} + \sum D_o)) \quad (3)$$

where inputs are from emissions (E_w), atmospheric inputs ($f_A D_A$), transport from sediment ($f_S D_{SW}$; diffusion and resuspension) and the summation of advective flows from adjacent segments ($\sum f_{wi} D_i$). Losses from water are by transformation or volatilization ($f_w D_w$), loss to sediment by particle deposition and diffusion ($f_w D_{ws}$) and the sum of advective flows to adjacent segments ($\sum f_w D_o$).

Table 2. Process D-values and rate expressions used in the fate model.

Processes	D values (mol/Pa.h)	Rates (mol/h)
Sediment Burial	D_1 or D_B	$G_B.C_S$ or $(G_B.Z_S).f_S$ or $D_1.f_S$
Sediment Transformation	D_2 or D_S	$V_S.C_S.k_S$ or $(V_S.C_S.k_S).f_S$ or $D_2.f_S$
Sediment Resuspension	D_3 or D_R	$G_R.C_S$ or $(G_R.C_S).f_S$ or $D_3.f_S$
Sediment to Water Diffusion	D_4 or D_T	$K_T.A_S.C_S/K_{SW}$ or $(K_T.A_S.Z_W).f_S$ or $D_4.f_S$
Water to Sediment Diffusion	D_4 or D_T	$K_T.A_S.C_W$ or $(K_T.A_S.Z_W).f_W$ or $D_4.f_W$
Sediment Deposition	D_5 or D_D	$G_D.C_P$ or $(G_D.Z_P).f_W$ or $D_5.f_W$
Water Transformation	D_6 or D_W	$V_W.C_W.k_W$ or $(V_W.Z_W.k_W).f_W$ or $D_6.f_W$
Volatilization	D_7 or D_V	$K_V.A_W.C_W$ or $(K_V.A_W.Z_W).f_W$ or $D_7.f_W$
Absorption	D_7 or D_V	$K_V.A_W.C_A/K_{AW}$ or $(K_V.A_W.Z_W).f_A$ or $D_7.f_A$
Water Outflow	D_J	$G_J.C_W$ or $(G_J.Z_W).f_W$ or $D_J.f_W$
Water Particle Outflow	D_Y	$G_J.C_P$ or $(G_J.Z_P).f_W$ or $D_Y.f_W$
Rain Dissolution	D_9 or D_M	$G_M.C_A/K_{AW}$ or $(G_M.Z_W).f_A$ or $D_9.f_A$
Wet Particle Deposition	D_{10} or D_C	$G_C.C_Q$ or $(G_C.Z_Q).f_A$ or $D_{10}.f_A$
Dry Particle Deposition	D_{11} or D_Q	$G_Q.C_Q$ or $(G_Q.Z_Q).f_A$ or $D_{11}.f_A$
Water Inflow	D_i	$G_i.C_i$ or $(G_{ij}.Z_W).f_i$ or $D_i.f_i$
Water Particle Inflow	D_X	$G_X.C_X$ or $(G_X.Z_P).f_i$ or $D_X.f_i$
Direct Emission	-	E_W

Notes:

Groups in parentheses are D values (mol/h.Pa), e.g. D_1 is $(G_B.Z_S)$. Z values are fugacity capacities (mol/m³.Pa). The rate is the product of D and fugacity i.e. Df.

G values are flow rates (m³/h) of a phase, e.g. G_B is the sediment burial rate.

C represents concentration in sediment (S), water (W), air (A), aerosol (Q), water particles (P), water inflow (i), water particle inflow (X), water outflow (J) and particle outflow (Y).

f_W , f_S , f_A , and f_i are fugacities of water, sediment, air, and water inflow.

k_W and k_S are water and sediment transformation rate constants (h⁻¹).

K_{SW} is equivalent to the ratio of Z values in the two compartments (Z_S/Z_W) and is a dimensionless sediment-water partition coefficient. K_{AW} is Z_A/Z_W , dimensionless air-water partition coefficient.

K_T is sediment-water mass transfer coefficient and K_V is the water side overall mass transfer coefficient (m/h).

A_W and A_S are the surface areas for the air-water and water-sediment interfaces (m²). V_W and V_S are the water and sediment compartment volumes (m³).

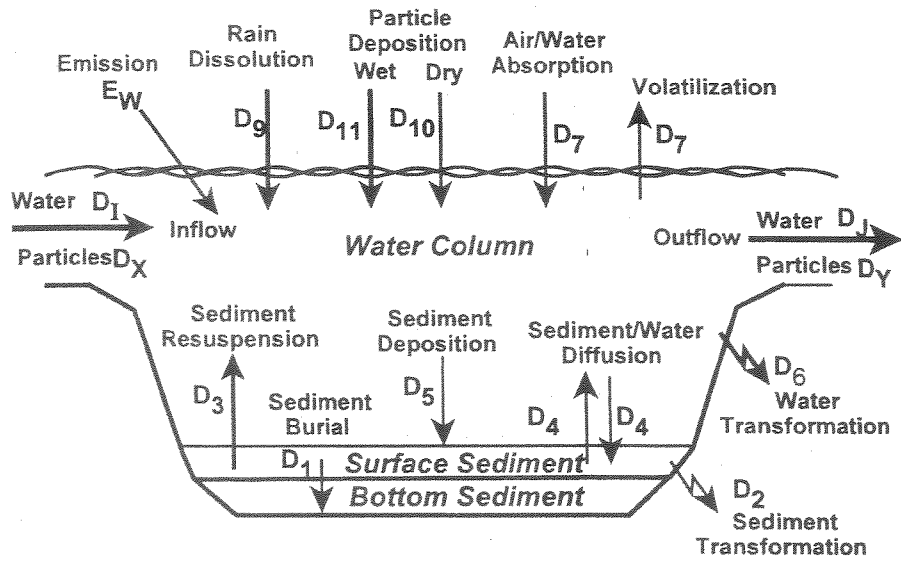


Figure 3. Processes treated in each QWASI model segment.

Thus, for water compartments

$$df_W = \frac{dt}{VZ} * ((E_W + f_A D_A + f_S D_{SW} + \sum f_{wi} D_i) - f_W (D_W + D_{WS} + \sum D_O)) \quad (3)$$

where inputs are from emissions (E_W), atmospheric inputs ($f_A D_A$), transport from sediment ($f_S D_{SW}$; diffusion and resuspension) and the summation of advective flows from adjacent segments ($\sum f_{wi} D_i$). Losses from water are by transformation or volatilization ($f_W D_W$), loss to sediment by particle deposition and diffusion ($f_W D_{WS}$) and the sum of advective flows to adjacent segments ($\sum f_W D_O$).

For sediment compartments

$$df_S = \frac{dt}{VZ} * ((f_W D_{WS}) - f_S (D_{SW} + D_S)) \quad (4)$$

where inputs are from transport from water to sediment ($f_W D_{WS}$) by particle deposition and diffusion, and losses are by diffusion and particle resuspension to water ($f_S D_{SW}$) and by burial or transformation ($f_S D_S$). Note that a number of D values presented in Table 2 are consolidated in these equations to simplify their presentation and the speed of calculations.

Using these equations, the change in fugacity in each segment compartment is calculated over a small time step. The changes in chemical mass, concentration and fluxes to and from each compartment can then be calculated. These calculations are repeated, with periodic output, until the end of the simulation time is reached. An overall chemical mass balance is compiled over the duration of the simulation and checked for consistency.

2.3. Parameters, Baseline Values, Uncertainty, Sensitivity

Known and estimated characteristics of the model segments are listed in Table 3. Total surface areas of the four segments, as defined in figure 1, were estimated using a geographic information system (GIS). The salt marsh system is subject to tidal water flows with a period slightly greater than 12 hours. The average tidal amplitude measured at a gauge located at the mouth of Purvis Creek is 2.4 m (NOAA, 2000). Efforts to use GIS to calculate the volume and flux of water moving through the marsh with each tidal cycle were hampered by the lack of detailed elevation data for the marsh relative to the nearest tidal gauge. Because of this, we decided to take a simpler approach for modeling water flow through the marsh by treating the marsh segments like a river system with a fixed volume and a continuous flow of water through each segment. Water volumes were estimated to reflect the average water volume in each segment over a tidal cycle, while flow rates were estimated to reflect tidal flows. The average water volume for the LCP (segment 3) and Lower (segment 4) marsh segments were estimated based on an assumed average water depth of 0.1 m over a tidal cycle (L. DiPinto, personal communication). It was also assumed that the entire water volume in these segments would be replaced with each tidal cycle, thus yielding a replacement time of 12 hours. For segments one and two, water volume calculations also included consideration of the water in the creek channel. Average creek depth was estimated to be 4.5 m in segment one and 1.7 m in segment two based on GIS analysis (described below). Based on GIS analysis, the creeks make up 95.5% and 64.3% of the average volume of these segments respectively. Water residence times for these segments exceed 12 hours because some water remains in the creeks at low tide.

Depths for Purvis Creek were determined from a National Oceanic Service (NOS) bathymetric chart (hardcopy). Two depth readings were used from this chart - one at the mouth of the creek just west of the small island (9 feet), and one immediately east of the island (14 feet). These depths are based on a datum of Mean Low Low Water (MLLW) and thus represent depths at MLLW. To estimate depths at Mean High High Water (MHHW), the tidal range for the closest tide gauge (East River, 7.8 feet) was used. Thus the estimated MHHW depths for the points listed above are 16.8 and 21.8 feet, respectively. At the headwater of the creek, a MHHW depth of 0.0 feet was used. Purvis Creek water depths between the point east of the island (21.8 feet) and the headwaters (0.0 feet) were interpolated and assigned by the GIS at approximately 100m interval points along the centerline of the creek. A rasterized topographic surface (5 meter cellsize) of the channel was then generated using the depth points as inputs. The raster surface was then converted to points using the centroid of each 5 m grid. A triangulated irregular network (TIN) surface was then created from the points and was used to estimate water volumes in the creek. Areas outside of the main channel as well as the island at the mouth were excluded from the volumetric analysis for the creek. The volume at MHHW was calculated using a vertical datum of 0.0 feet and the volume at MLLW was calculated using a vertical datum of 7.8 feet (2.377m) to account for the tidal range. Based on these calculations, the marsh system receives an average water flow of 44,587 m³/h from the Turtle River to segment 1, of which 53% flows into the other three segments and 47% remains in segment 1. Water mixing between segments 3 and 4 was assumed to occur at a rate equivalent to 10% of the flowrate between segments 1 and 3. Segment 2 was assumed to exchange water only with segment 1 because of a causeway built between segments 2 and 3. Outflow from the marsh all runs through segment 1 and back to the Turtle River.

No information was available on the suspended particle concentration in water from the marsh or Turtle River, thus a default baseline value of 3 mg/L was used. The organic fraction of suspended particles, which is typically larger than they are in bulk sediments, was estimated based on the measured organic content of surficial sediment particles in salt marshes near North Inlet, South Carolina (Sharma et al. 1987; Morris and Bradley, 1999). Sediment particle density (2 kg/L), sediment volume fraction particles (*i.e.* 1 - porosity; 0.35), and mixing depth (0.05 m) were also estimated from these studies.

Table 3. Physical and hydrological characteristics of the Purvis Creek salt marsh used as baseline values in the LCP-QWASI model.

Parameter	Marsh Segments				Source
	Purvis Creek (1)	Upper (2)	LCP (3)	Lower (4)	
Surface area (m ²)	300004	837608	178392	333594	GIS analysis
Mean water depth (m)	1.53	0.25	0.1	0.1	estimated
Mean water volume (m ³)	459524	212602	17839	33359	calculated
Water residence time (h)	12.9	15	12	12	calculated
Suspended particles (mg/L)	3	3	3	3	estimated
Organic fraction	0.2	0.2	0.2	0.2	estimated ¹
Sediment particle density (kg/L)	2	2	2	2	estimated ¹
Organic fraction	0.02	0.06	0.08	0.06	measured ¹
Vol. fraction sediment solids	0.35	0.35	0.35	0.35	estimated ¹
Sediment active depth (m)	0.05	0.05	0.05	0.05	estimated ¹
Sedimentation rate (g/m ² /d)	8	8	8	8	estimated
Resuspension rate (g/m ² /d)	3	3	3	3	estimated
Burial rate (g/m ² /d)	4	4	4	4	estimated
<u>Hydrologic Balance (m³/h)</u>					
Tributary	Turtle River				
River Inflow	44587				calculated
River Outflow	44587				calculated
<u>Inter-segment Flows</u>					
to 1	-----	19385	1487	2780	calculated
to 2	19385	-----	0	0	calculated
to 3	1487	0	-----	149	calculated ²
to 4	2780	0	149	-----	calculated ²

¹ Sharma et al. 1987; Morris and Bradley, 1999.

² Flow between segments 3 and 4 estimated to be 10% of flow between segments 1 and 3.

Sediment particle organic fractions were average values calculated from available data for each segment of the Purvis Creek marsh derived from a CD-ROM database originally developed by GeoSyntec Consultants (1999a,b).

There are no data on the rates of sediment particle deposition, resuspension or burial for the Purvis Creek marsh. Sharma et al (1987) measured average net sediment accumulation rates ranging from 1.4 to 4.5 mm/yr in a North Carolina salt marsh. They note that the similarity between these rates and the average rate of sea level rise (~3.0 mm/yr; Kjerfve et al 1978) would suggest that their measurements are probably typical for most salt marshes on the Atlantic coast. A net sedimentation rate of 3.0 mm/yr equates to a rate of about 5 g/m²/d based on the particle density and sediment volume fraction noted above. Estimated rates of 8.0 g/m²/d for the gross deposition rate and 3.0 g/m²/d for the particle resuspension rate are assumed as default values in the model based on professional judgement and experience at other sites. The burial rate is estimated to be 4.0 g/m²/d (or 80% of the net particle deposition rate of 5.0 g/m²/d) to account for the mineralization of organic carbon in settled particles (i.e., from an organic fraction of 0.2 in newly settled particles to 0.02 to 0.08 in sediment particles). These are critical model parameters and will be subject to a sensitivity analysis.

2.4. Chemical Characteristics

Table 4 gives the physical chemical properties at 25°C and estimated environmental half lives in air, water and sediment for the Aroclor 1268 mixture and for three representative PAHs. The three PAHs were selected to encompass the broad range of chemical structures in this class (i.e., from tri-cyclic phenanthrene to the penta-cyclic benzo-a-pyrene). Physical chemical properties for the three PAHs are from Mackay et al. (1992). The average properties for the Aroclor 1268 mixture were also estimated from this source using a homolog composition of 5% hexa-, 10% hepta-, 45% octa-, 35% nona- and 5% deca- chlorinated congeners and average molecular weight of 453 (Kannan et al. 1997).

While physical chemical properties are considered as constants, there is some degree of error associated with their measurement. A recent study by de Maagd et al. (1998) provides insight on the error associated with measurements of log Kow and water solubility for nine PAHs, including several of the selected compounds. For log Kow, the 95% confidence limits were generally in the range of ±0.1 to ±0.2 of the mean (e.g. B(a)P log Kow 6.13, 95% confidence limits 5.91-6.28, n=6). When expressed as log values this degree of error appears small, but the ratio of upper/lower confidence limits for Kow is about a factor of two. Given this level of uncertainty associated with Kow measurements for individual chemicals, agreement within a factor of two between observed concentrations and model results should be considered good. Water solubilities were measured in the same study with appreciably greater consistency, with standard deviations averaging about 15% of the mean value. The uncertainty associated with the Aroclor 1268 property values will be greater still because it is a mixture and because of the difficulties in measuring these properties for extremely hydrophobic chemicals.

The half life values for environmental degradation of the PAHs (Table 4) represent selected values from Mackay (1992) with the recognition that true values may vary by a factor of 3 to 5. The environmental degradation half life values for Aroclor 1268 were selected to reflect recent studies that support the view that PCB degradation rates are negligible in most environmental systems, particularly for highly chlorinated congeners (Connolly et al. 2000; U.S. EPA. 1997).

Table 4. Physical and chemical properties of selected chemicals at 25°C and their estimated degradation half lives (hours) in air, sediment and water. All values for PAHs are from Mackay et al (1992). The basis for the Aroclor 1268 values are described in the text.

Property	Chemical			
	Aroclor 1268	Benzo(a)pyrene	Fluoranthene	Phenanthrene
Melting pt. (°C)	177.0	175.0	111.0	101.0
Molecular wt. (g/mol)	453.0	252.3	202.3	178.2
Water solubility (g/m ³)	0.0030	0.0076	0.5200	2.2000
Vapor pressure (Pa)	5.0x10 ⁻⁵	2.8.0x10 ⁻⁶	0.005	0.072
log Kow	7.7	6.04	5.22	4.57
<u>Estimated Half life (hours)</u>				
Air	55000	170	170	170
Water	2.0x10 ⁶	1700	1700	1700
Sediment	2.0x10 ⁶	55000	55000	55000

Average starting sediment chemical concentrations were calculated from an inverse distance weighted surface using a GIS database for all sample points collected in each of the four marsh segments prior to the emergency sediment removal conducted by the U.S. EPA (termed “pre-removal” concentrations; Table 5). Post-removal sediment concentrations were calculated in the same manner for marsh segment 3 (LCP segment) using data collected after the removal process was completed. Starting sediment concentrations in the other three segments were assumed to be unaffected by the removal process. Each surface was generated using the average concentration within the top 10 cm at each sample point. For the surface generation, a radius of 100m (with no minimum or maximum number of sample points used) and an exponent of 3 was used to control the significance that surrounding points had upon the interpolated value. In addition, a barrier separating segment 2 (upper marsh) from the other segments was used in the interpolation process. The cell size used was 5 m.

Aroclor 1268 concentrations from water samples (1 L unfiltered) collected in the marsh were highly variable, ranging from below the detection limit (<280 ng/L) to 360 ng/L in the upper marsh (segment 2), 670 to 66,000 ng/L in segment 3, and below detection in the lower marsh (segment 4) and lower Purvis Creek (segment 1) (figure 3.4b Stratus report). The model is quite insensitive to the initial segment water concentrations as they adjust quickly to reflect the concentration in the underlying sediment, hence a uniform initial water concentration of 4 ng/L was selected. Total PAH concentration measurements in water are not available; a starting concentration of 5 ng/L was selected for all segments in the fate simulations. There are no data on the “background” concentrations of either Aroclor 1268 or the PAHs in the Turtle River. Background concentrations for the Turtle River can have an effect on simulation results; as is discussed below.

Table 5. Pre-removal and post-removal chemical concentrations in sediments (ng/g dw) of the Purvis Creek salt marsh used as initial values in model simulations.

Parameter	Marsh Segments			
	Purvis Creek (1)	Upper (2)	LCP (3)	Lower (4)
<u>Pre-removal sediments</u>				
Aroclor 1268	4260	3678	76585	6817
Total PAHs	192	429	587	535
<u>Post-removal sediments</u>				
Aroclor 1268	4260	3678	5476	6817
Total PAHs	192	429	457	535

Data source: GeoSyntec Consultants (1999a,b).

2.5. Outline of Simulations

An initial simulation for Aroclor 1268 was run for a 30 year period using the baseline parameter values and pre-removal sediment concentrations described above. Changes in chemical concentration and mass for each segment are presented along with analysis of the importance of the various fate and transport pathways including burial and transport to the Turtle River. This was followed by limited sensitivity and uncertainty analyses which focus on parameters affecting the key transport and fate pathways. The impact of the removal of the highly contaminated sediments from segment 3 on the long-term fate and export of Aroclor 1268 to the Turtle River was then examined by comparing simulations initiated with the pre- and post-removal sediment concentrations. The discussion identifies data requirements that would aid in reducing model uncertainty.

Simulations for the selected PAHs are more illustrative owing to the lack of measured sediment and water concentrations for specific chemicals in the various segments of the marsh. The approach taken was to model the fate of total PAHs using the physical chemical properties of three common PAHs which differ considerably in structure and properties (Table 4) and compare the results. The results focus on comparing the relative importance of the various fate and transport pathways rather than the absolute changes in chemical mass or concentration in the system.

2.6. Results and Discussion

This fate model was designed to examine three main issues; the overall fate of the selected chemicals in the marsh system both pre- and post-removal; the extent to which these chemicals move to the adjoining Turtle River; the likely water and sediment concentrations that organisms would be exposed to over time. These issues are addressed in detail for Aroclor 1268, including a limited sensitivity and uncertainty analysis on key model parameters. The analysis for PAHs is less detailed, largely owing to the more limited data for this group of chemicals.

2.6.1. Aroclor 1268 Baseline Results

Prior to the sediment removal efforts, the marsh system is estimated to have had a burden of about 710 kg of Aroclor 1268 in the top five cm of sediment plus a minute amount in the overlying water. About 67.3% of the burden was in segment 3, 15.2% in segment 2, 11.2% in segment 4, and the remaining 6.3% in segment 1. An additional unquantified mass of Aroclor 1268 would have been in the deeper sediments but is not considered to be part of the active system (i.e., not available for exchange with the overlying sediment layer in the model). Without sediment removal, and no new inputs of Aroclor 1268 to the system, the total mass in the active system and concentrations in sediment and water

show a near uniform rate of decline with an overall half life of 14.6 years (Figure 4). The half lives in individual segments range from 13.4 years for segment 1 to 15.3 years for segment 4. The predicted sediment concentrations follow from the initial concentrations entered into the model, whereas the predicted water concentrations are dependent upon the underlying sediment concentrations. In this simulation, the predicted water concentrations in the first year range from 3.8 ng/L in segment 1 to 81 ng/L in segment 3. These values compare favorably with the few field-measured concentrations. The short water residence time in all segments prevents the water from equilibrating with the elevated sediment concentrations. Examination of water and sediment fugacities reveals that the water only reaches between 3% and 14% of the potential equilibrium concentration. This results from the combination of the rapid flushing of the system with relatively uncontaminated water from the Turtle River and the slow net flux from the sediment.

Examination of chemical flux rates in the simulation reveals the relative importance of the various processes in regulating the decline in the mass and concentration of Aroclor 1268 in sediments and its export to the Turtle River. The flux rates (g/d) shown in Figure 5 are for all four segments combined and were calculated from data from a point one year into the simulation. Burial accounts for 88.2% of the loss of Aroclor 1268 from the surface sediments, followed by transformation/degradation (6.4%), net particle exchange with overlying water (5.3%), and diffusion to the water column (0.07%). The burial rate is driven by overall sediment particle dynamics including net sedimentation rate, respiration of sediment organic carbon, and sediment mixing processes (mixing depth, bioturbation, storm events). While the model treats burial below the mixing depth of 5 cm as a removal process, the chemical remains in the marsh system and has the potential (in reality) to return to the surface layer where it would be considered bioavailable. However, this process is not considered in this preliminary model. The loss rate by degradation is estimated to be close to that by transport to overlying water despite using a long half life (2×10^6 hours or 228 years).

Of the 4.76 g/d net flux from sediment to the overlying water, 84.5% (4.03g) is exported to the Turtle River by advection. Most of the remaining amount (15.5%) is lost to the atmosphere by volatilization. These results suggest that particle dynamics also control the rate of Aroclor 1268 export to the Turtle River. While there are reasonable estimates of net sedimentation rates for salt marshes from the general area (Sharma et al. 1987), there are no data on gross particle deposition rates or resuspension rates. Over the first 20 years of the simulation, an estimated 19,620 g of Aroclor 1268 are exported to the Turtle River at an average rate of 981 g/year (range 1510 g in the first year to about 600 g in year 20). This process accounts for just 4.5% of the loss from the system. The importance of the Purvis Creek marsh as a source of PCBs to the Turtle River cannot be determined further without knowledge of the characteristics of the larger system and other sources of PCBs to the Turtle River.

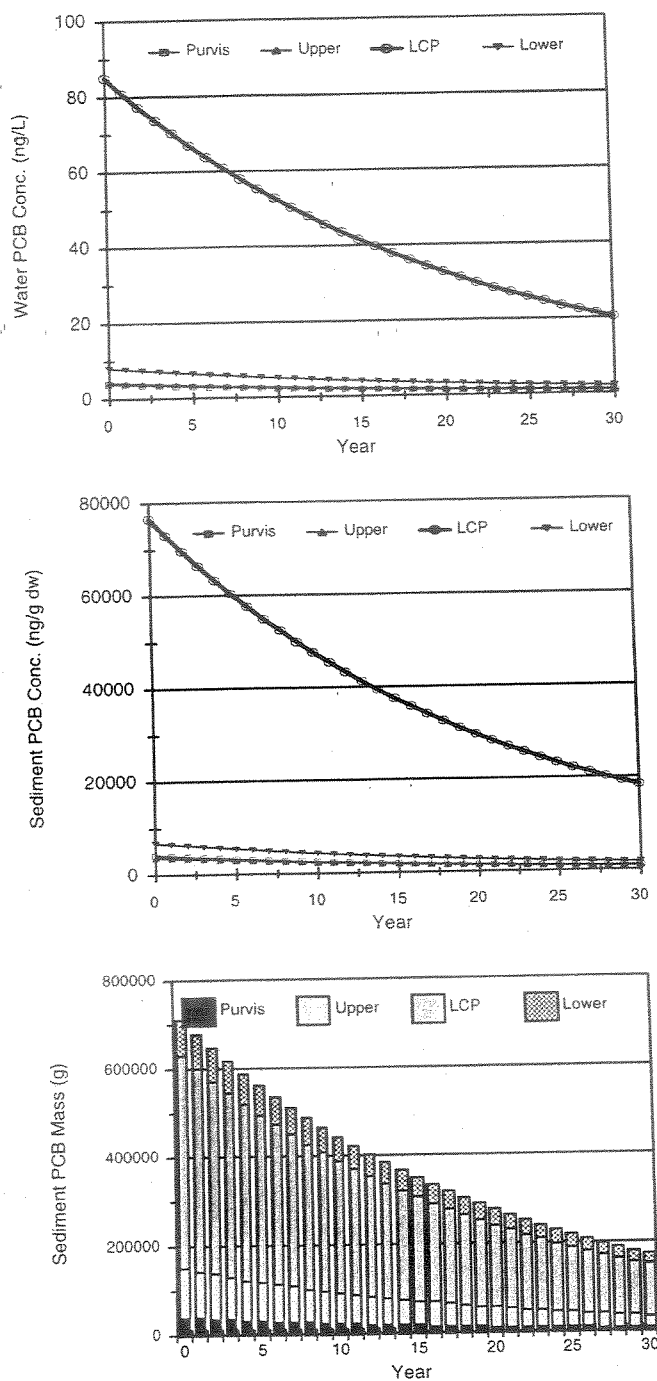


Figure 4. Simulated changes in Aroclor 1268 concentrations in sediment and water of each model segment and mass in the sediments using the baseline data set and pre-removal sediment concentrations.

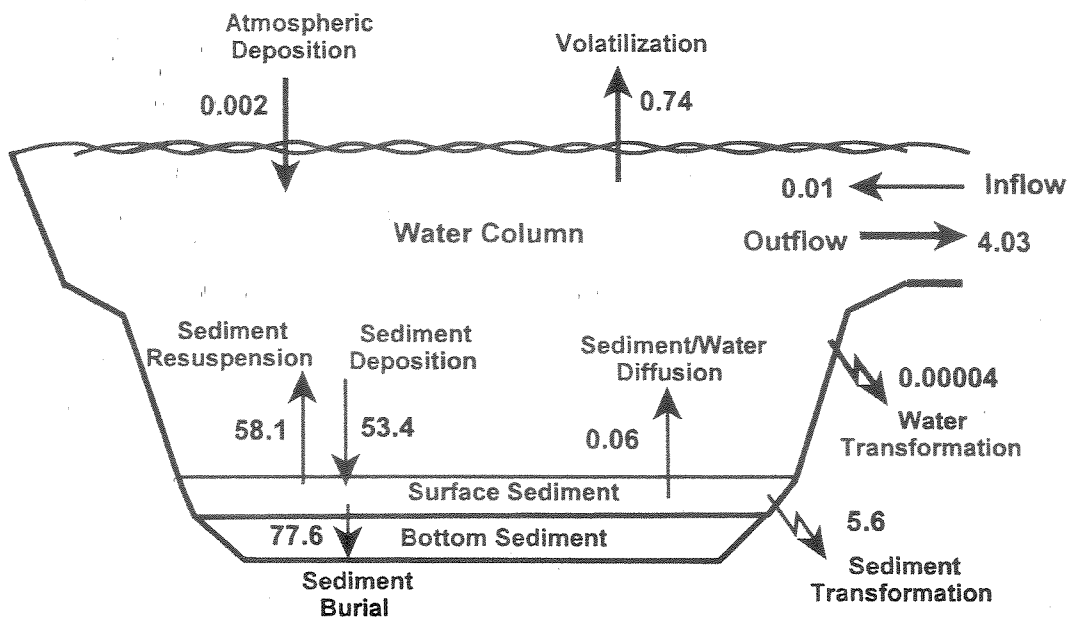


Figure 5. Overall flux rates of Aroclor 1268 (g/day) for the four combined segments after one year of the simulation using the baseline data set.

2.6.2. Sensitivity / Uncertainty Analysis

This analysis centers on the parameters that define sediment dynamics and, hence, processes of burial and particle resuspension. These parameters were examined both on their own and in groups (e.g. high and low sedimentation scenarios). Sediment mixing depth, suspended particle concentration and organic carbon fraction and background Aroclor concentrations in air and incoming river water were also examined. We selected the overall sediment half life and the 20-year average rate of Aroclor export to the Turtle River as meaningful measures of model response to changes in the selected parameters (Table 6). The sensitivities of these model outputs to changes in parameter values are expressed in this table as the ratio of the relative percent changes in the output value over the relative percent change in the input parameter value. A sensitivity index value of 0 indicates that the particular model output is unaffected by a change in the input parameter. An index value of 1.0 indicates that the model output responds in proportion to the change in the particular input value. A value of -1.0 indicates that the model output is negatively proportional to the change in the input value.

Sediment Dynamics

The high and low sedimentation scenarios represent a 50% increase and decrease, respectively, from the selected baseline values for the three parameters describing sediment dynamics. Overall half life was strongly influenced by these changes; increasing by 79% (to 26.2 years) under low sedimentation conditions and decreasing by 31% (to 10.1 years) under high sedimentation. The effects on export to the Turtle River were more modest; increasing by 9.1% under low and decreasing by 11.7% under high sedimentation conditions. Examining parameters individually confirmed that the half life is particularly sensitive to changes in the burial rate, particularly lower rates. The sediment mixing depth also has a near-proportional influence on overall half life, primarily by changing the mass of chemical subject to burial. The changes in predicted export rates to the Turtle River are nearly proportional to the changes

made in the particle resuspension rates, indicating that these processes are tightly connected. As noted earlier, there is considerable uncertainty associated with this parameter. Sediment mixing depth and the burial rate have less influence on the export process.

Sediment Particles

Changes in the suspended particle concentration or their organic carbon content had very little influence on overall half life. Changes in the organic carbon content had very little influence on either the half life or on the export rate to the Turtle River. The latter outcome can be explained by considering that any increase in particle capacity to bind hydrophobic chemicals and export them by advective flow would be balanced by an increase in chemical flux to the sediments with settling particles. In contrast, a change in the concentration of suspended particles without a change in sedimentation rate results in near-proportional changes in the rate of export to the Turtle River. Field data on suspended particle concentrations and their organic carbon content would be useful for reducing model uncertainty since about 90% of Aroclor 1268 in water is associated with particles.

Background Concentrations

The baseline background air and incoming river water concentrations were set at very low concentrations (0.014 ng/m³ air, 0.01 ng/L water) which are equal when expressed as fugacities (i.e. they are in equilibrium). These background levels are about 4,000-fold lower (or 0.00025x) than the fugacity of the initial sediment concentration from the upper marsh segment. We adjusted the background air and water concentrations to 400x (5.63 ng/m³, 3.91 ng/L), 40x (0.563 ng/m³ air, 0.391 ng/L) and 4x (0.0563 ng/m³, 0.0391 ng/L) higher than the baseline air and water concentrations to examine the effect of these parameters on model outcome. These values are about equal to 0.1, 0.01 and 0.001 of the upper marsh sediment fugacity.

Increasing the background concentrations of Aroclor 1268 by factors ranging from four to 400x had very little influence on the overall half life in the marsh because half life is primarily driven by the burial rate. Four- and forty-fold increases in background concentrations had little effect on the average net export rate to the Turtle River largely because the incoming river water concentration remains well below that of the marsh outflow. A 400-fold increase in the background levels did reduce the average export rate because the Aroclor 1268 concentration in incoming river water was initially close to and eventually exceeded the outflowing concentration. Atmospheric exchange processes are insignificant for Aroclor 1268 under all of these scenarios. Field data on the concentrations of PCBs and other chemicals of interest in the Turtle River would be useful for refining our estimates of chemical transport from the marsh.

Summary

Although these simulations do not constitute a formal uncertainty analysis, they do provide a rough indication of the range of predicted values for Aroclor 1268 half life and the average export rate. The mean overall half life from all simulations given in Table 6 was 15.6 years (sd = 4.9; range 9.0 to 27.4 years), while the mean export rate was 930 g/year (sd = 327; range 275 to 1481). Model uncertainty for Aroclor 1268 could be reduced by having better data on sediment dynamics, suspended particle concentrations and background chemical concentrations for the Turtle River.

Table 6. Results of limited sensitivity /uncertainty analysis for Aroclor 1268 in the dynamic LCP-QWASI model.

Parameter	Values	Overall Sediment Half Life		Mean Export Rate to Turtle River †	
		years	sensitivity	g/yr	sensitivity
<u>Sediment Dynamics</u>					
"baseline" sedimentation (g/m ² /d)					
- sedimentation	8.0	14.6	--	981	--
- resuspension	3.0				
- burial	4.0				
resuspension rate (g/m ² /d)	1.5	15.0	-0.05	501	0.98
	4.5	14.2	-0.05	1451	0.96
burial rate (g/m ² /d)	3.0	18.7	-1.12	1076	-0.39
	5.0	11.9	-0.74	901	-0.33
sediment mixing depth (cm)	3.0	9.0	0.96	771	0.54
	10.0	27.4	0.88	1201	0.22
high (+50%) sedimentation (g/m ² /d)					
- sedimentation	12	10.1	-0.62	866	-0.23
- resuspension	4.5				
- burial	6.0				
low (-50%) sedimentation (g/m ² /d)					
- sedimentation	4.0	26.2	-1.59	1071	-0.18
- resuspension	1.5				
- burial	2.0				
<u>Suspended Particles</u>					
concentration (mg/L)	1.0	15.0	-0.04	421	0.86
	5.0	14.2	-0.04	1481	0.76
fraction organic carbon	0.1	14.5	0.01	1031	-0.10
	0.3	14.6	0.00	966	-0.03
background concentrations*	400x	14.6	0.00	2.75	< -0.01
(multiples of baseline air and water	40x	14.6	0.00	912	< -0.01
concentrations)	4x	14.6	0.00	980	< -0.01

† Average net export rate of Aroclor 1268 over first 20 years of simulation

* Refer to text for explanation.

2.6.3. Post-Removal Simulation

Results of the post-removal simulation are presented in Figure 6 and compared to the pre-removal simulation in Table 7. The sediment removal program lead to an estimated 62.5% reduction in the total Aroclor 1268 inventory in the top 5 cm of the sediments of the Purvis Creek marsh. Area-weighted average sediment and model-estimated water concentrations were reduced by 62.5% and 64.9% respectively. By removing the most contaminated sediments from segment 3 the removal program also greatly reduced the spatial heterogeneity in exposure concentrations. Sediment removal was estimated to result in a slight reduction in the overall half life for Aroclor 1268 in the marsh, with half lives decreasing in segments 1, 2 and 4 and increasing in segment 3. These changes can be attributed to the reduced transport of Aroclor 1268 from segment 3 to the other segments. It is likely that these small changes in half life would be undetectable in a monitoring program. It is estimated that the removal program will lead to a 34% reduction in the long-term (20 year) average rate of Aroclor 1268 export to the Turtle River. Export to the Turtle River is a relatively minor loss process from the marsh in both the pre-removal (4.5%) and post-removal (5.9%) simulations, while burial remains the dominant loss process (~85% in both cases).

Table 7. Summary of results from the pre-removal and post-removal fate model simulations for Aroclor 1268. Note that combined concentrations for sediment and water are area-weighted means.

	Segment 1	Segment 2	Segment 3	Segment 4	Combined
<u>Pre-removal</u>					
initial sediment conc (ng/g dw)	4260	3678	76585	6817	12300
sediment burden (kg)	44.7	107.9	477.8	79.5	709.9
initial water conc (ng/L)	3.8	4.1	81.0	7.8	13.1
sediment half life (yrs)	13.4	15.1	14.6	15.3	14.6
20 yr average export (g/yr)	---	---	---	---	981
<u>Post-removal</u>					
initial sediment conc (ng/g dw)	4260	3678	5476	6817	4615
sediment burden (kg)	44.7	107.9	34.2	79.5	266.3
initial water conc (ng/L)	2.6	3.9	6.0	7.4	4.6
sediment half life (yrs)	11.9	14.1	14.9	14.8	14.1
20 yr average export (g/yr)	---	---	---	---	646

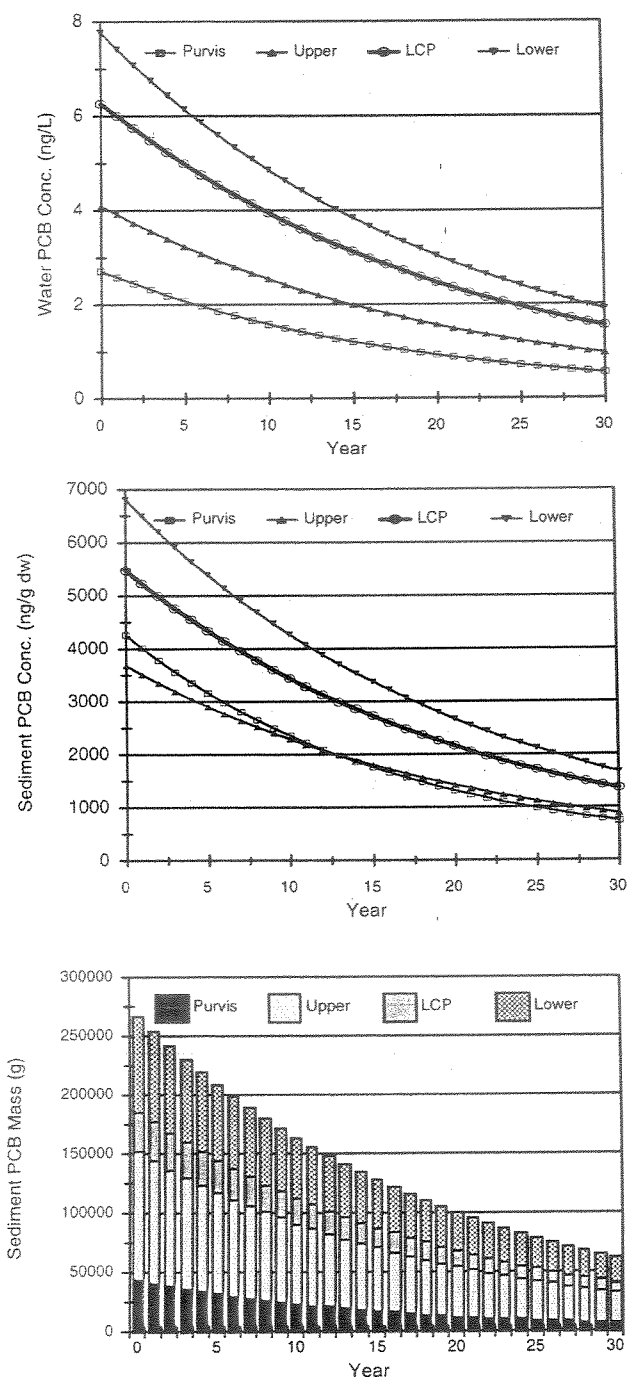


Figure 6. Simulated changes in Aroclor 1268 concentrations in sediment and water of each model segment and mass in the sediments using the baseline data set and post-removal sediment concentrations.

2.6.4. PAH Results

A summary of the simulations for the three example PAH compounds initiated with the pre-removal sediment concentrations is given in Table 8 and Figure 7. The system is estimated to have a burden of 24.5 kg of total PAH in the top five cm of sediment plus a small amount in the overlying water. Total PAHs are predicted to have a much shorter overall half life than Aroclor 1268 in Purvis Creek Marsh, with estimates ranging from 3.1 years for phenanthrene to 4.4 years for the heavier and more hydrophobic benzo(a)pyrene. This results from the PAHs having a much shorter assumed degradation half life in sediments (6.3 years) than Aroclor 1268 (228 years). The differences in half life between the three example PAHs can be attributed to their partitioning properties between sediment, water and air. Burial and particle resuspension are consistently less important sediment loss processes than reaction, while diffusion to overlying water is only significant for the more water soluble, lower molecular weight PAHs such as phenanthrene. In the water column, the low molecular weight PAHs such as phenanthrene tend to be lost from the system by advection and, to a lesser extent, by volatilization. With increasing molecular weight (and log Kow), PAHs in the water column increasingly cycle back to the sediments with settling particles, thus reducing their loss by advection.

Because of the short half life of total PAHs in the marsh, estimates of PAH export rates over time are highly sensitive to the background concentrations used for air and particularly the inflow water from the Turtle River. For the baseline simulations shown here (Table 8; Figure 7) we used background air and water concentrations equivalent to 0.01 of the fugacity of the segment 3 pre-removal sediments (429 ng/g dw). These background concentrations were:

5.5 ng/m³ air and 4.7 ng/L water for phenanthrene
0.4 ng/m³ air and 1.1 ng/L water for fluoranthene
0.03 ng/m³ air and 0.2 ng/L water for benzo(a)pyrene

These estimated background water concentrations are only 1.5- to 3.6-fold lower than the predicted initial water concentrations for the three example PAHs in the Purvis Creek segment (segment 3) which has direct water exchange with the Turtle River. As the burden of PAHs in the marsh declines over time, the PAH concentration in the marsh outflow water eventually drops below the incoming background concentration, and the Turtle River becomes a source of PAHs to the marsh. In these simulations, the outflow concentrations fall below the inflow concentrations after 8.6 years for phenanthrene, 14.5 years for fluoranthene and 16.7 years for benzo(a)pyrene. This contributes to the low 20-year average net export rates to the Turtle River. Selecting other background concentrations will affect export rate predictions but have relatively little effect on the overall half life.

The sediment removal program had very little effect on sediment PAH concentrations in segment 3 (Table 5). Over the entire marsh, the removal program is estimated to have reduced the PAH sediment burden in the top 5 cm from 24.5 kg to 23.7 kg, a reduction of less than 4%. Thus, simulations initiated with the post-removal PAH sediment concentrations yield virtually identical results to those described above and are not reported here.

Model uncertainty for PAHs could be reduced by refining degradation half life values (particularly in sediments), by modelling specific PAHs, and having better data on background chemical concentrations for the Turtle River.

Table 8. Summary of the simulations for the three example PAHs using baseline model values and initiated with the pre-removal sediment concentrations. The relative importance of loss processes are illustrated using output values combined from the four segments from the end of the first simulation year. Loss processes are shown as flux rates (g/d) and percent loss by the various processes for sediment and the water column.

	Phenanthrene	Fluoranthene	Benzo(a)pyrene
Overall half life (years)	3.1	3.9	4.4
Export to Turtle River - 20 yr. average (g/year)	105	132	56
<u>Loss Rates from Marsh (g/d)*</u>			
Burial	2.2	2.3	2.4
Reaction (sediment + water)	6	6.2	6.3
Volatilization	1.4	0.2	0.003
Advective Outflow	7.7	2.6	0.74
Total Loss Rate (gross)	17.3	11.3	9.44
Total Loss Rate (net)	12.2	10.1	9.21
<u>Sediment Loss Processes (%)</u>			
Burial	17.6	21.3	22.5
Reaction	46.8	56.5	59.6
Resuspension	13.2	16	16.9
Diffusion to water	22.3	6.1	1
<u>Water Loss Processes (%)</u>			
Sedimentation	4.6	22.2	64.9
Advection (gross)	80.1	71.6	34.6
Volatilization	14.6	5.6	0.1
Reaction	0.6	0.6	0.3

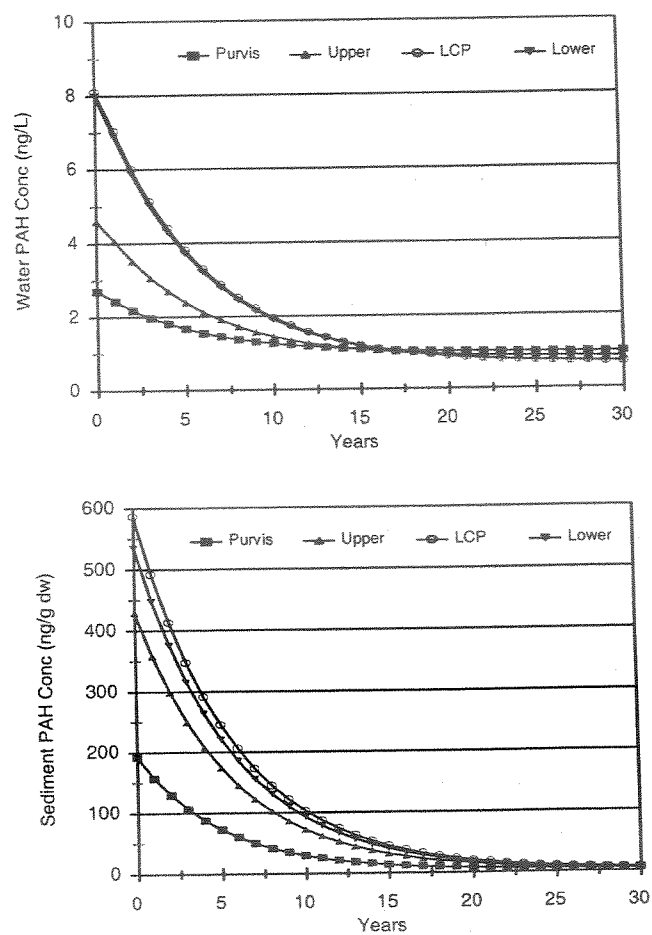


Figure 7. Simulated changes in total PAH concentrations in sediment and water of each model segment using the physical chemical properties of fluoranthene.

3.0. Bioaccumulation Modelling

A spreadsheet version of the Gobas (1993) steady-state food web bioaccumulation model calibrated for the Lake Ontario food web was obtained from the web site www.rem.sfu.ca/toxicology. No major structural changes were needed to adapt the model to the Purvis Creek Salt Marsh food web. The only changes were to increase the number of species considered, and to the model variables describing the chemicals, the environmental characteristics, the species and their feeding preferences. Data requirements for the model are given in Table 9. Species feeding preferences and the structure of the simplified food web for the Purvis Creek Salt Marsh used in the preliminary model simulations are described in Table 10 and Figure 8. The majority of species included in the simplified food web derive their energy from benthic sources, hence it is expected that the sediments will be a more important source of chemicals to the food web than the overlying water. The steady-state structure of the model necessitates the assumption that all organisms are exposed continuously to concentrations specified for a particular simulation. Considering the size of the marsh and the variability of sediment contaminant concentrations within the system, it is likely that some of the larger and more mobile species, such as blue crab and red drum, routinely violate this assumption. The heterogeneity in sediment concentrations at the site may also make it difficult to calculate meaningful BSAF values for at least some species. Simulation results for Aroclor 1268 are compared to field-measured tissue concentrations and BSAFs ($\text{ng/g lipid} \div \text{ng/g sediment organic carbon}$). The lack of measured PAH concentrations in biota from the Purvis Creek Marsh precludes comparisons to simulation results for the three selected PAHs.

Table 9. Data requirements for running the Gobas (1993) food web bioaccumulation model.

Characteristics	Comments
<u>Chemical Characteristics</u>	
- octanol water partition coefficient (K_{ow})	- taken from Table 4
- concentration in water (ng/L)	- chemical concentrations from field data or model predictions (refer to text)
- concentration in sediment (ng/g dry wt)	
<u>Environmental Characteristics</u>	
- organic carbon content of water (kg/L)	- calculated from values used in fate model $= 6.0 \times 10^{-7} \text{ kg/L}$
- organic carbon content of sediment (%)	- average of values from Table 3 (5.5%)
- density of organic carbon and lipid (kg/L)	- used default value from Gobas (0.9 kg/L)
<u>Organism Characteristics</u>	
<i>Pelagic phytoplankton and zooplankton</i>	
- lipid content	- assumed a value of 2%
<i>Benthic infauna</i>	
- lipid content	- assumed a value of 4%
<i>Larger organisms</i>	
- wet weight (g), lipid content (%)	- refer to Table 10
- feeding preferences (% of diet that is species i)	- refer to Table 10
- growth rate (d^{-1})	- used default rate from Gobas (0.00133 d^{-1})
- biotransformation rate constant (d^{-1})	- assume value of 0 d^{-1} for Aroclor 1268 - refer to text for PAHs

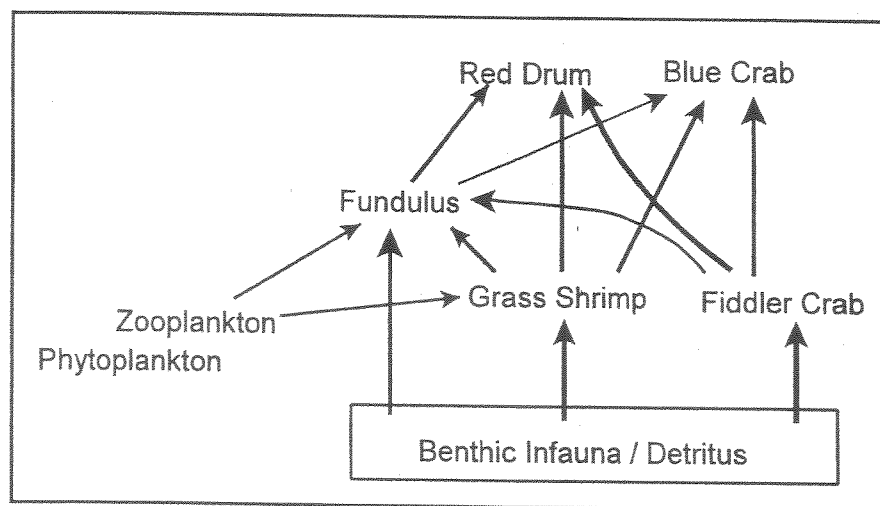


Figure 8. Structure of the simplified food web for the Purvis Creek Salt Marsh used in the preliminary model simulations.

Table 10. Species characteristics and feeding preferences used in the preliminary model simulations based on summaries from the Marine and Coastal Species Information System (MACSIS, 1998) and Sprenger et al (1997).

Species	Feeding Preferences
Phytoplankton 2% lipid (assumed)	n/a
Zooplankton 4% lipid (assumed)	n/a
Benthic Infauna (<i>mixed species</i>) 3% lipid (assumed)	n/a
Fiddler Crab (<i>Uca sp.</i>) 3% lipid, 0.5 g wet wt (average)	100% benthic infauna
Grass Shrimp (<i>Palaemonetes pugio</i>) 2% lipid, 2.0 g wet wt	20% pelagic zooplankton, 80% benthic infauna
Killifish (<i>Fundulus heteroclitus</i>) 2% lipid, 7.0 g wet wt	20% pelagic zooplankton, 40% benthic infauna 30% fiddler crab, 10% grass shrimp
Blue Crab (<i>Callinectes sapidus</i>) 3% lipid, 150 g wet wt	20% benthic infauna, 30% fiddler crab 40% grass shrimp, 10% killifish
Red Drum (<i>Sciaenops ocellatus</i>) 4% lipid, 500 g wet wt	10% benthic infauna, 25% fiddler crab 25% grass shrimp, 40% killifish

3.1. Bioaccumulation of Aroclor 1268.

The linear nature of the food web model dictates that the chemical concentrations predicted in all organisms will be proportional to any changes in the exposure concentrations so long as the ratio of sediment to water concentrations remains constant. Because of this, it is useful to examine the predicted sediment:water concentration ratios from the fate model simulations for Aroclor 1268 (Figure 9). For the simulation initiated with pre-removal sediment concentrations, the ratio in the four segments falls in the range between 830:1 and 1075:1 over the 30 year simulation period. This ratio is essentially constant over time for three of the four model segments (Upper, Lower and LCP segments), with values ranging between 830:1 and 900:1. In the remaining segment (Purvis Creek), a linear decline from 1075:1 to 990:1 is predicted over the 30 year simulation. A similar pattern is evident from the post-removal simulation with a virtually constant ratio of about 900:1 for the Upper, Lower and LCP segments, and a ratio declining from 1570:1 to 1350:1 over the 30 years in the Purvis Creek segment.

Varying the sediment:water concentration ratio over the range of 800:1 to 1600:1 by altering the water concentrations of Aroclor 1268 had virtually no effect on the BSAFs predicted by the model (Figure 10). This shows that the predicted concentrations in organisms are almost entirely driven by the sediment concentrations. Furthermore, it suggests that a single set of BSAF values can be applied to predict the changes in organism concentrations as the sediment concentrations decline over time. A ratio of 900:1 was adopted as a model baseline value for subsequent simulations.

Figure 10 also shows that measured Aroclor 1268 BSAFs for Carolina marsh clam (*Polymesoda caroliniana*, filter feeding benthic infauna) (Kannan 1999), grass shrimp, striped mullet (*Mugil cephalis*, an herbivore and benthivore) and sea trout (*Cynoscion nebulosus*, an omnivore) from Purvis Creek (Maruya and Lee 1998a) are considerably lower than the model-predicted BSAFs for benthos, grass shrimp and other fish species. While some of the discrepancy may be attributed to factors such as species mobility or spatial heterogeneity in sediment concentrations, the Gobas model may also overpredict BAFs and BSAFs for superhydrophobic chemicals ($\log K_{ow} > 7.0$) such as Aroclor 1268. It does not include any mechanisms which could account for the negative relationship between BSAF and $\log K_{ow}$ for the superhydrophobic Aroclor 1268 congeners observed by Maruya and Lee (1998a) and Kannan (1999) in the Purvis Creek marsh. The Thomann model (1992), in contrast, does include provisions (i.e. lower gill uptake efficiency) for the reduced bioaccumulation of superhydrophobic chemicals, but they have not been validated with experimental data (Burkhard, 1998). For subsequent simulations in this preliminary modeling exercise we added a factor to the Gobas model to reduce the Aroclor 1268 BSAF for the benthic infauna from 1.0 (i.e. assumed equilibrium partitioning) to a value of 0.4 which reflects the negative relationship between BSAF and $\log K_{ow}$ for superhydrophobic contaminants in a number of studies (Tracey and Hansen 1996; Maruya and Lee 1998a; Kannan 1999). No changes in gill or dietary uptake efficiencies were made for any other organisms. This simple revision effectively reduced the predicted BSAFs for all organisms, except the pelagic phytoplankton and zooplankton, by a factor of about 2.5 (Figure 11). More extensive revisions to the model would require a detailed review of the bioaccumulation of superhydrophobic chemicals.

Three simulations were conducted with the revised bioaccumulation model using sediment concentrations reflecting the range of Aroclor 1268 levels observed in the Purvis Creek Marsh (Figure 12): 4,260 ng/g (Purvis Creek segment 1); 12,300 ng/g (area-weighted pre-removal marsh average; and 76,600 ng/g (LCP marsh, segment 3 pre-removal) Included in Figure 12 are measured total PCB concentrations for organisms collected at various locations within the Purvis Creek marsh prior to sediment removal (Sprenger et al 1997; Maruya and Lee, 1998a,b; Kannan et al. 1997; Kannan 1999). The model predictions overlap measured concentrations for benthos (i.e. periwinkle data from Sprenger et al, 1997; clam data from Kannan 1999), fiddler crab, killifish and one observation for blue crab (from Kannan et al 1997). Some observations for killifish and blue crab fall well below the range of predicted

concentrations, as do the measured concentrations for grass shrimp and red drum. Measured concentrations for these organisms do, however, show good agreement with concentrations predicted for pelagic phytoplankton and zooplankton which are based on equilibrium partitioning with the freely dissolved water concentration. The same holds true for several other species that were not included in the model food web (brown shrimp *Panaeus aztecus*, spot *Leiostomus xanthurus*, striped mullet *Mugil cephalus*, and sea trout *Cynoscion nebulosus*). There are two possible explanations for this, neither of which can be addressed adequately by the current model. First, superhydrophobic chemicals, such as Aroclor 1268, may not biomagnify to the same extent as less hydrophobic PCBs and Aroclor mixtures. This is partly addressed by the reduction in BSAF to 0.4 for the benthic infauna discussed above. Second, the concentrations observed in many marsh organisms may be a function of their habitat ranges which include contaminated and relatively clean areas (i.e. the biota sampled did not live or feed exclusively in the LCP marsh area). Further interpretation of the contaminant data for biota is also hindered by imprecise descriptions of sampling locations within the marsh.

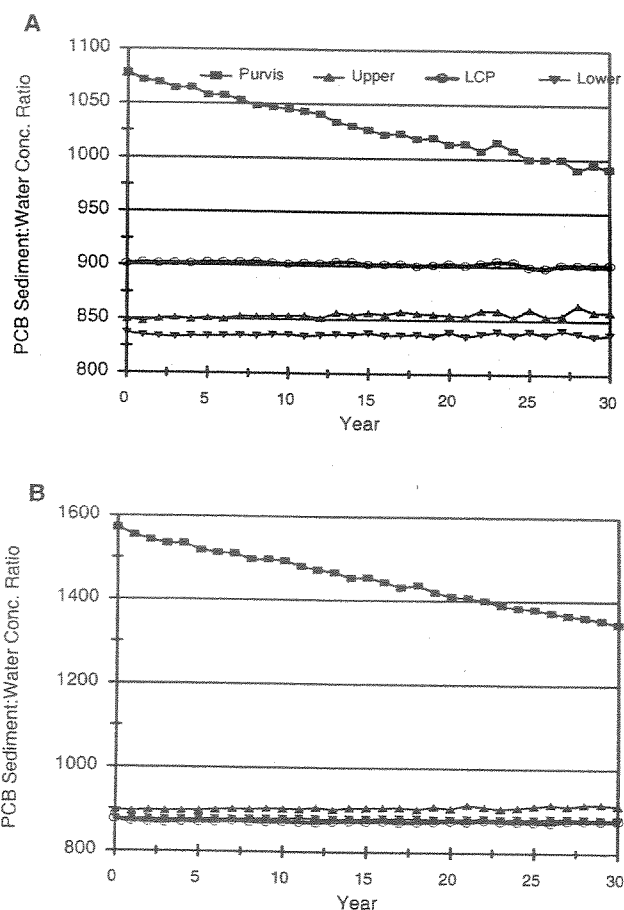


Figure 9. Predicted sediment:water concentration ratio ($\text{ng/g sediment dry wt} \div \text{ng/L water}$) from the baseline fate model simulations for Aroclor 1268 initiated with the (A) pre-removal, and (B) post-removal sediment concentrations.

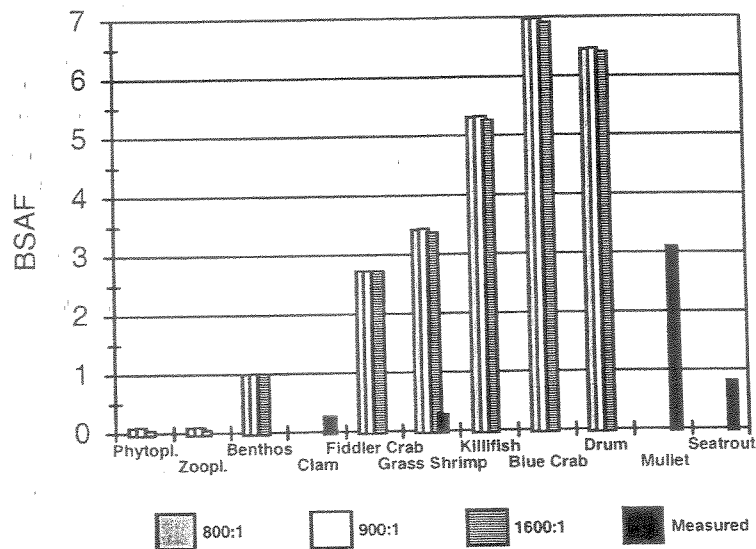


Figure 10. The effect of varying the sediment:water concentration ratio (ng/g sediment dry wt ÷ ng/L water) by altering the water concentrations on the model-predicted BSAFs for Aroclor 1268. Measured BSAFs reported by Maruya and Lee (1998a) and Kannan (1999) for four species from Purvis Creek are included for comparison.

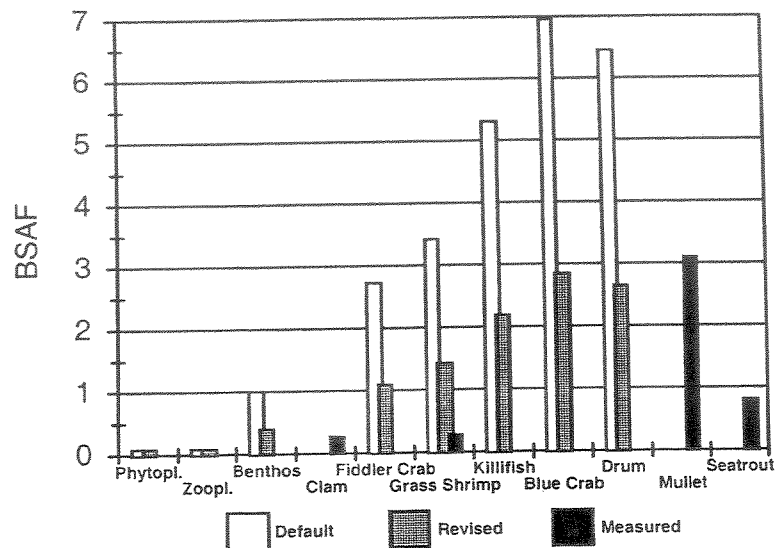


Figure 11. Predicted Aroclor 1268 BSAF values for organisms in the simplified salt marsh food web assuming equilibrium partitioning for benthic infauna (default Gobas model; BSAF = 1.0) and assuming a reduced BSAF of 0.4 for benthic infauna (revised model).

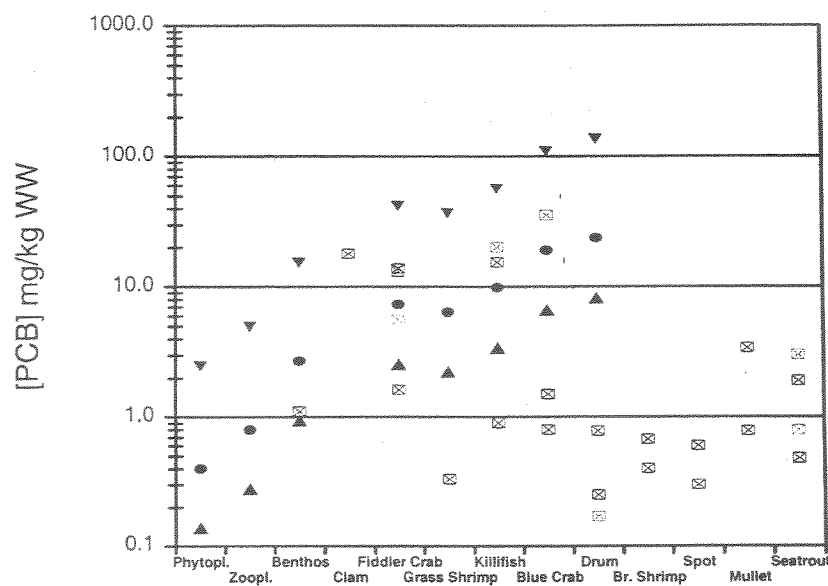


Figure 12. Comparison of predicted tissue concentrations with concentrations measured in organisms (□) from various locations in the Purvis Creek marsh. Sediment Aroclor 1268 concentrations used in the three simulations were: 4260 ng/g dw (▲) - reflecting concentrations in Purvis Creek; 12,300 ng/g dw (●) - reflecting the average (weighted by segment area) pre-removal concentration for the entire marsh; 76,600 ng/g dw (▼) - reflecting the pre-removal concentration in segment 3. A 900:1 sediment:water concentration ratio was used in the simulations.

3.2. Bioaccumulation of PAHs

PAHs have the potential to bioaccumulate in invertebrates and fish by both food ingestion and water respiration pathways. This potential to bioaccumulate is mitigated in many species by their capacity to enzymatically metabolize many PAHs to more soluble oxygenated species which are more readily excreted than the parent compounds. The concentration achieved in an organism is the result of a balance being achieved between input rates (as dictated by respiration and feeding) and output rates which are largely dependent on metabolic capability supplemented by egestion and respiration losses.

BSAFs have been reported for a variety of PAHs for both marine and freshwater species. A considerable proportion of these studies report BSAFs calculated on a wet weight or dry weight basis for both tissue and sediment, thus making the results more difficult to interpret and compare. Of the literature reviewed that report lipid and organic carbon normalized BSAFs for PAHs, nearly all values were at or below values predicted from equilibrium partitioning theory. For example, BSAFs for total PAH in the marine clam *Macoma balthica* and in the polychaete *Nereis succinea* ranged between 0.4 and 2.2 for several sites in Chesapeake Bay (Foster and Wright, 1988). BSAFs for the freshwater benthic isopod *Asellus aquaticus* ranged between 0.1 and 0.4 for 12 PAHs, while the BSAF for naphthalene was 4.7 (van Hattum et al, 1998). In both studies BSAFs were not related to log Kow and there were significant outlier values of BSAF at some field locations. BSAFs between blue mussels (*Mytilus edulis*) and seston particles calculated on a lipid-to-lipid basis from a study by Broman et al. (1990) did not exceed 0.21 for six of the selected PAHs. The highest BSAF was for chrysene (0.21) and the lowest was for benzo(a)pyrene (0.04). Overall, there is no evidence that PAHs biomagnify in benthic organisms and in fact are often found at concentrations much lower than would be expected from equilibrium

partitioning. This is consistent with findings that many benthic species, but not all, have enzyme systems capable of transforming PAHs. Bioavailability from sediments, feeding strategy and ability to metabolize PAHs are the most important factors influencing PAH BSAFs (Varanasi et al. 1985).

Many studies have examined the capacity of a broad range of aquatic and marine species to metabolize PAHs. Several comprehensive reviews have been published (Varanasi, 1989; van Brummelen et al, 1998; de Maagd and Vethaak, 1998). In many of the studies, whole-organism half-lives or rate constants for metabolism are not reported, nor can they be calculated from the information provided. Much of the early literature is based on studies with radio-labelled compounds and report tissue concentrations as percent of activity from parent compound versus metabolites. While such studies provide an indication of a species' ability to metabolize the particular compound, or possibly PAHs in general, useful rate constants cannot be derived easily. More recent studies focus on the enzyme systems involved in PAH metabolism, namely the cytochrome P450 family involved in Phase I oxidation reactions and the Phase II conjugation enzymes. Studies have been conducted on mammals, birds, fish, and invertebrates with attention to the tissue distribution of enzymes, substrate-specific activity and induction, and to quantifying metabolite production, some of which are carcinogenic (e.g. B(a)P-dihydrodiols). As with earlier studies, most enzyme-based studies do not describe results in terms of whole-body half-lives or elimination rate constants. For example, there are no direct means of relating measures of enzyme activities for PAH biotransformation (e.g. pmol/mg protein/min), which are measured *in vitro*, to the whole organism.

In general, rates of PAH biotransformation in fish are higher than in invertebrates, but it is difficult to generalize within taxonomic groups, even between closely related species. This is perhaps especially true among invertebrates, where some species such as *Daphnia* and *Diporeia* display little if any capacity to biotransform PAHs. The lack of an extensive database on PAH biotransformation rates by aquatic organisms, or the ability to predict rates based on structure, poses a considerable challenge in modelling their bioaccumulation by individual organisms and through food webs.

The approach taken here was to first model the three example PAHs assuming no metabolism and using the average measured sediment PAH concentration from across the four marsh segments (435 ng/g dw). The water concentrations used in these simulations were derived from the initial sediment:water concentration ratio derived from the fate model (Figure 13). A second set of simulations was then run using the same exposure conditions which included PAH metabolism by fish using rate constants based on elimination half-life values for 700g rainbow trout measured by Niimi and Palazzo (1986). It was assumed that there was no PAH metabolism by invertebrates in these simulations. A third set of simulations used the same metabolism rate constant values, but were based on sediment and water concentrations derived from the fate model five years into the simulations described previously. Conditions for these simulations are summarized in Table 11. A lack of data prevents any comparisons between simulation results and measured PAH concentrations in organisms from the Purvis Creek marsh. This also limits our ability to refine or calibrate the model any further at this time.

Niimi and Palazzo (1986) reported overall half-lives of 9 days for phenanthrene, 6 days for fluoranthene and about 2 days for benzo(a)pyrene in rainbow trout. Rate constants for metabolism for red drum were adjusted iteratively in the model to give overall half-lives equivalent to the measured trout values for each of the three PAHs. The same rate constant values were also assigned to killifish. These values are summarized in Table 11. Note that no metabolism was required to match the overall half life for phenanthrene.

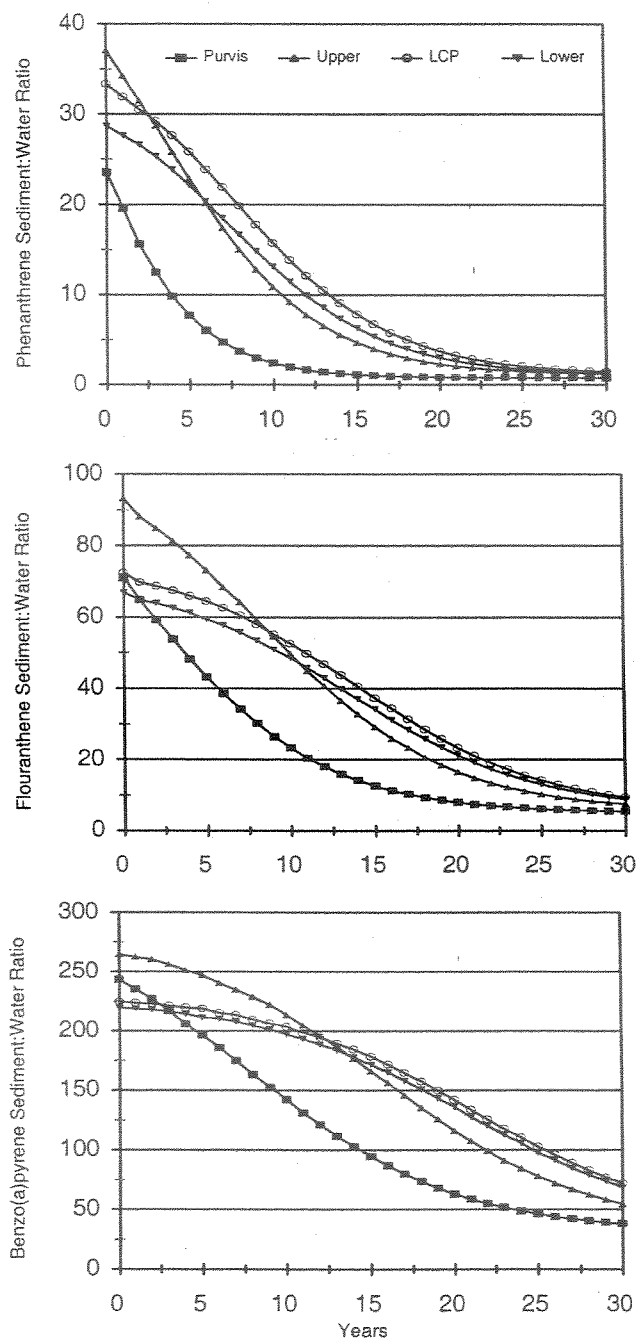


Figure 13. Predicted sediment:water concentration ratios (ng/g sediment dry wt ÷ ng/L water) for the three example PAHs derived from the baseline fate model simulations initiated with the pre-removal sediment concentrations.

Table 11. Summary of conditions used in the food web bioaccumulation model simulations for the three PAHs. Note that the same metabolism rate constant value (km) was used in simulations B and C for each chemical.

Chemical / Simulation	Csed (ng/g dw)	Cw ng/L	Csed:Cw	Species	km (d ⁻¹)	Overall t _{1/2} (d)
<u>Phenanthrene</u>						
- simulation A (no metabolism)	435	15.5	28:1	killifish red drum	--- ---	0.8 7.6
- simulation B	435	15.5	28:1	killifish	0.0	0.8
- simulation C	114	6.3	18:1	red drum	0.0	7.6
<u>Fluoranthene</u>						
- simulation A	435	6.0	72:1	killifish red drum	--- ---	3.2 22.4
- simulation B	435	6.0	72:1	killifish	0.085	2.3
- simulation C	150	2.6	57:1	red drum	0.085	6.0
<u>Benzo(a)pyrene</u>						
- simulation A	435	1.8	235:1	killifish red drum	--- ---	12.6 43.9
- simulation B	435	1.8	235:1	killifish	0.33	1.8
- simulation C	168	0.8	210:1	red drum	0.33	2.0

Results for the PAH simulations are presented in Figure 14. Predicted concentrations of phenanthrene show little evidence of bioaccumulation through the food web. Benthic infauna are predicted to have higher concentrations than all other organisms because they are assumed to be in equilibrium with sediment phenanthrene concentrations. The similarity in concentrations between all other organisms indicates that the aqueous exposure pathway is more important than dietary exposure for low molecular weight (low log Kow) PAHs such as phenanthrene. The predicted decline in tissue concentrations over five years (average 65%) lay between the predicted decline in water concentrations (59%) and sediment concentrations (74%).

The simulations for fluoranthene suggest that there is some potential for bioaccumulation through the food web but, like phenanthrene, the highest predicted concentrations are in benthic infauna. The higher concentrations in larger organisms, such as blue crab and red drum, are the result of both aqueous and dietary exposure pathways. The simulations that include metabolism demonstrate the impact that this parameter can have on model predictions and the uncertainty associated with modeling the accumulation of PAHs. The predicted declines in organism concentrations over five years (average 62%) are intermediate between the predicted average declines in water (56%) and sediment (65%) concentrations, further demonstrating that organism concentrations are dependent on both aqueous and dietary exposure pathways. The simulations for benzo(a)pyrene suggest that there is considerable potential for bioaccumulation and biomagnification through the food web so long as it is not metabolised by any organism. Accumulation is primarily via the diet with a maximum potential BSAF of 3.0 for red drum.

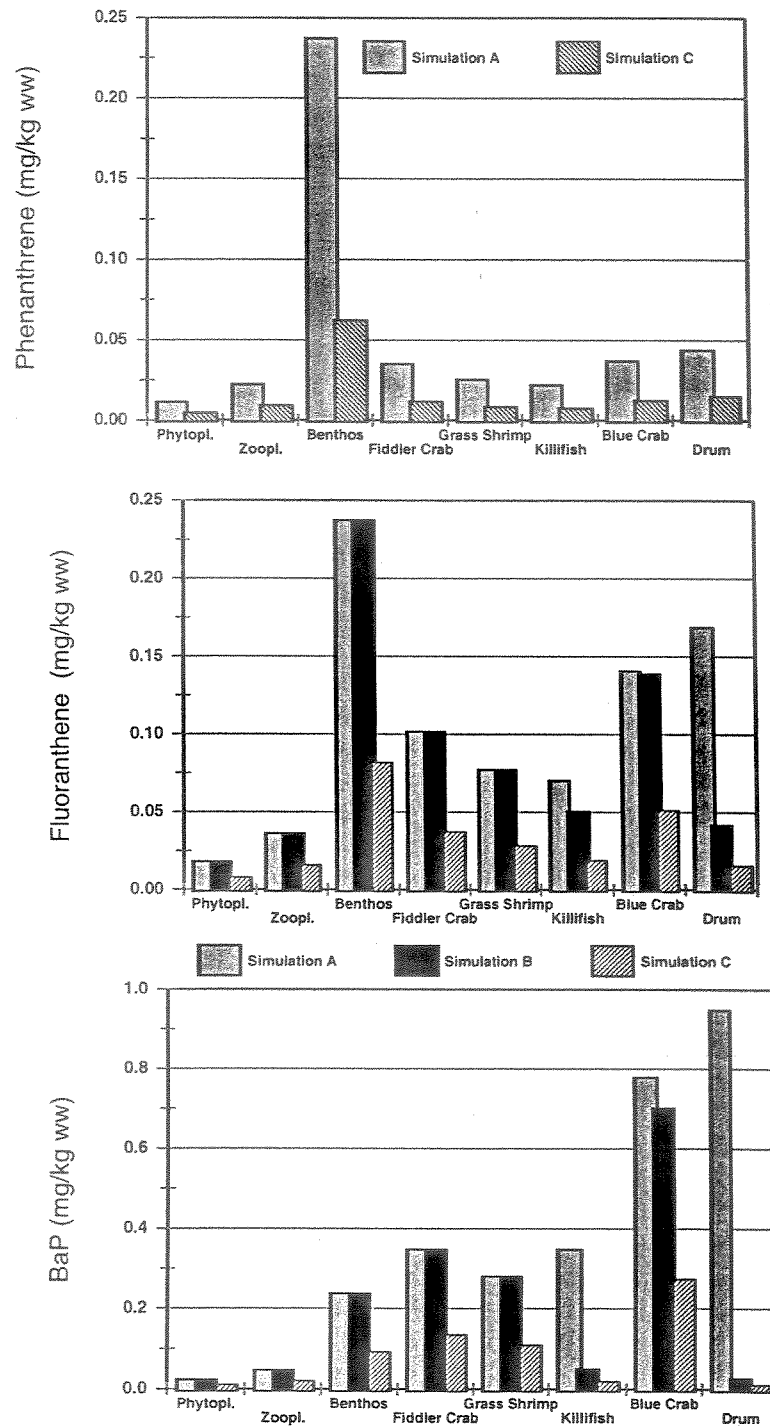


Figure 14. Predicted concentrations of phenanthrene, fluoranthene and benzo(a)pyrene for organisms in the Purvis Creek marsh derived from the simulations outlined in the text and Table 11.

The addition of PAH metabolism by killifish and red drum has significant effects on predicted concentrations in these species (e.g., BSAF for drum with metabolism drops to 0.1), and secondary effects on concentrations in their predators. For example, the concentration in blue crab is predicted to decline by about 10% because of the effect of metabolism on the concentration in killifish which constitutes 10% of the diet of crabs in these simulations. The predicted declines in organism concentrations over five years (average 60%) is similar to the predicted declines in sediment (61%) and water (57%) concentrations.

Simulations with fluoranthene and benzo(a)pyrene demonstrate the significant effects that metabolism can have on the accumulation of PAHs. There is considerable uncertainty associated with selecting appropriate rate constants for metabolism, particularly for invertebrate species. The simulations which excluded metabolism entirely may be viewed as worst case scenarios in any assessment for PAHs. Combining simulations with and without metabolism may be quite useful because they can provide estimates of the intake rate of these chemicals and the rate of formation of metabolites which may be toxicologically important.

4.0. Conclusions

Preliminary fate and food web bioaccumulation models were developed for the Purvis Creek marsh and applied to Aroclor 1268 and three example PAHs representing a range of physical chemical properties. The dynamic fate model was used to predict the environmental half life of these chemicals in the marsh, the potential for export to the adjoining Turtle River, and the change in water and sediment concentrations over time. An overall half life of 14.6 years (range of 9.0 to 27.4 years under the simulations run) was predicted for Aroclor 1268 in the active marsh system, which was driven primarily by the rate of sediment burial in the marsh. Export to the Turtle River appears to be a relatively minor loss process, accounting for about 4.5% of the losses over a 20 year period (an average of 981 g/yr). Additional data on the particle and sediment dynamics in the marsh would be useful in reducing uncertainty in model predictions for Aroclor 1268.

The predicted overall half lives for the example PAHs were much shorter than for Aroclor 1268, ranging from 3.1 to 4.4 years. For all three PAHs degradation in sediment was the dominant loss process. The relative importance of other loss processes was dependent on physical chemical properties of each chemical. Export to the Turtle River was a minor loss process for all three example PAHs, with 20 yr average export rates ranging from 56 to 132 g/yr. The greatest source of uncertainty in modeling the PAHs was in the selection of degradation half life values (particularly in sediments). Model uncertainty would also be reduced by having better data on background chemical concentrations for the Turtle River.

The Gobas (1993) steady-state bioaccumulation model was adapted to a simplified salt marsh food web that included five species for which monitoring data for PCBs are available. No monitoring data for PAHs were found. The Gobas model appears to overpredict the bioaccumulation of superhydrophobic chemicals such as Aroclor 1268. A simple modification was thus made to the model to reduce the bioavailability of sediment Aroclor 1268 to benthic infauna by 60%. With this modification, observed PCB concentrations for four species were in reasonable agreement with the range of concentrations predicted by the model. The model, however, overpredicted concentrations in red drum by more than an order of magnitude, and would probably also overpredict concentrations in a number of other species (e.g., sea trout, striped mullet) if they were included in the model. This could be due to the current difficulties in modeling the accumulation of superhydrophobic chemicals, but could also be due to the mobility of these species (i.e., their ability to move to and from the marsh).

Simulations of the bioaccumulation of the PAHs showed the effects that a range of physical chemical properties (i.e., log Kow) can have on the potential accumulation of these chemicals through a food web. PAHs are readily metabolized by many aquatic species, thus greatly reducing their bioaccumulation and transfer through food webs. There is considerable uncertainty associated with setting rate constants for metabolism owing to a lack of data, especially for invertebrate species. Simulations were run to demonstrate the effect that metabolism can have on model predictions for two of the example PAHs.

For both Aroclor 1268 and PAHs, concentrations in aquatic organisms in the salt marsh would be expected to respond rapidly to changes in sediment and water concentrations. From this, the half lives predicted by the fate model for these chemicals may also be applied to the organisms included in the food web model and other similar species.

5.0. References

- Broman D, C Naf, I Lundbergh and Y Zebuhr. 1990. An in situ study on the distribution, biotransformation and flux of polycyclic aromatic hydrocarbons (PAHs) in an aquatic food chain (seston - *Mytilus edulis* L. - *Somateria mollissima* L.) From the Baltic: An ecotoxicological perspective. *Environ Toxicol Chem.* 9:429-442.
- Burkhard, LP. 1998. Comparison of two models for predicting bioaccumulation of hydrophobic organic chemicals in a Great Lakes food web. *Environ Toxicol Chem.* 17:383-393.
- Campfens, J and D Mackay. 1997. Fugacity-based model of PCB bioaccumulation in complex aquatic food webs. *Environ Sci Technol.* 31:577-583.
- Connolly, JP, HA Zahakos, J Benamen, CK Ziegler, JR Rhea and K Russell. 2000. A model of PCB fate in the upper Hudson River. *Environ Sci Technol.* 34:4076-4087.
- de Maagd PGJ, DThEM ten Hulscher, H van den Huevel, A Opperhuizen and DTHM Sijm. 1998. Physicochemical properties of polycyclic aromatic hydrocarbons: Aqueous solubilities, n-octanol/water partition coefficients, and Henry's law constants. *Environ Toxicol Chem.* 17:251-257.
- de Maagd PGJ and AD Vethaak. 1998. Biotransformation of PAHs and their carcinogenic effects in fish. pp 265-309 In: *The Handbook of Environmental Chemistry. Vol. 3. Part J.* Neilson, AH (ed). Springer-Verlag Berlin Heidelberg.
- Foster GD and DA Wright. 1988. Unsubstituted polynuclear aromatic hydrocarbons in sediments, clams, and clam worms from Chesapeake Bay. *Mar Poll Bull.* 19:459-465.
- GeoSyntec Consultants. 1999a. Close-Out Report: Marsh and Railroad Area Removal Revision 0. LCP Chemicals - Georgia; Brunswick, Georgia. Prepared for LCP Site Steering Committee. October.
- GeoSyntec Consultants. 1999b. CD-ROM of data for sediments, soil, and water at the LCP Superfunds site. Arcview project compilation of EPA, PTI, and Allied Signal data.
- Gobas, FAPC. 1993. A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food webs: application to Lake Ontario. *Ecol Modelling.* 69:1-17.
- Kannan, K, KA Maruya and S Tanabe. 1997. Distribution and characterization of polychlorinated biphenyl congeners in soil and sediments from a superfund site contaminated with Aroclor 1268. *Environ Sci Technol.* 31:1483-1488.
- Kjerfve, B, MJ Klug, RJ Wiegert and AG Chalmers. 1978. Low frequency response of estuarine sea level to non-local forcing. p 497-513. In ML Wiley [ed.], *Estuarine Interactions*. Academic Press.
- Lun, R, K Lee, L DeMarco, C Nalwajko and D Mackay. 1998. A model of the fate of polycyclic aromatic hydrocarbons in the Saguenay Fjord. *Environ. Toxicol. Chem.* 17:333-341.
- Mackay, D. 1991. *Multimedia Environmental Models: The Fugacity Approach*. Lewis Publishers, Chelsea, MI. 257p.

- Mackay, D and BE Hickie. 2000. Mass balance model of source apportionment, transport and fate of PAHs in Lac Saint Louis, Quebec. *Chemosphere*. 41:681-692.
- Mackay, D, WY Shiu, and KC Ma. 1992. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Vol II. Lewis Publishers, Chelsea, MI. 597p.
- Mackay, D, M Joy, and S Paterson. 1983. A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in lakes. *Chemosphere*. 12:981-997.
- Mackay, D. 1989. An approach to modelling the long-term behaviour of an organic contaminant in a large lake: Application to PCBs in Lake Ontario. *J. Great Lakes Res.* 15:283-297.
- Mackay, D, and JM Southwood. 1992. Modelling the fate of organochlorine chemicals in pulp mill effluents. *Water Poll Research J Canada*. 27:509-537.
- Mackay, D. 1979. Finding fugacity feasible. *Environ Sci Technol*. 13:1218.
- MACSIS. 1998. Marine and Coastal Species Information System. www.fw.vt.edu/www/macsis.
- Maruya, KA and RF Lee. 1998a. Biota-sediment accumulation and trophic transfer factors for extremely hydrophobic polychlorinated biphenyls. *Environ Toxicol Chem*. 17:2463-2469.
- Maruya, KA and RF Lee. 1998b. Aroclor 1268 and toxaphene in fish from a Southeastern U.S. estuary. *Environ Sci Technol*. 32:1069-1075.
- Morris, JT and PM Bradley. 1999. Effects of nutrient loading on the carbon balance of coastal wetland sediments. *Limnol. Oceanogr*. 44:699-702.
- Niimi AJ and Palazzo V. 1986. Biological half-lives of eight polycyclic aromatic hydrocarbons (PAHs) in rainbow trout (*Salmo gairdneri*). *Water Res*. 20:503-507.
- NOAA. 2000. National Oceanographic and Atmospheric Administration (NOAA) Tide Tables. www.co-ops.nos.noaa.gov/tides/.
- Paterson, S, and D Mackay. 1985. The fugacity concept in environmental modelling. Pp.121-140 In: *The Handbook of Environmental Chemistry*, Vol. 2/Part C. Hutzinger, O. Ed. Springer-Verlag, Heidelberg.
- Sharma, P, LR Gardner, WS Moore and MS Bollinger. 1987. Sedimentation and bioturbation in a salt marsh as revealed by ^{210}Pb , ^{137}Cs and ^7Be studies. *Limnol Oceanogr*. 32:313-326.
- Sprenger, MD, NJ Finley and M Huston. 1997. Ecological risk evaluation of the salt marsh and adjacent areas at the LCP superfund site Brunswick, GA. Environmental Response Team Center. Office of Emergency and Remedial Response.
- Thomann, RV, JP Connolly and TF Parkerton. 1992. An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. *Environ Toxicol Chem*. 11:615-629.

- Tracey, GA and DJ Hansen. 1996. Use of biota sediment accumulation factors to assess similarity of non-ionic chemical exposure to benthically-coupled organisms of differing trophic mode. *Arch Env Contam Toxicol* 30:467-475.
- U.S. EPA. 1995. Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors. EPA-820-B-95-005.
- U.S. EPA. 1997. Phase 2 Report - Review Copy. Further Site Characterization and Analysis. Volume 2C - Data Evaluation and Interpretation Report. Hudson River PCBs Reassessment RI/FS. U.S. Environmental Protection Agency, Washington, DC. February.
- van Brummelen TC, B van Hattum, T Crommentuijn, and DF Kalf. 1998. Bioavailability and ecotoxicology of PAHs. pp 203-263 In: *The Handbook of Environmental Chemistry*. Vol. 3. Part J. Neilson, AH (ed). Springer-Verlag Berlin Heidelberg.
- van Hattum B, MJ Curto Pons, JF Cid Montanes. 1998. Polycyclic aromatic hydrocarbons in freshwater isopods and field-partitioning between abiotic phases. *Arch Environ Contam Toxicol*. 35:257-267.
- Varanasi U, WL Reichert, JE Stein, DW Brown, and HR Sanborn. 1985. Bioavailability and biotransformation of aromatic hydrocarbons in benthic organisms exposed to sediment from an urban estuary. *Environ Sci Technol*. 19:836-841.
- Varanasi U. 1989. *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*. CRC Press, Boca Raton, FL. 341p.